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ELEMENTS  
OF THE  
ART OF DYEING  
AND BLEACHING.

BY  
C. L. AND A. B. BERTHOLLET.

TRANSLATED FROM THE FRENCH,  
WITH NOTES AND ENGRAVINGS, ILLUSTRATIVE AND  
SUPPLEMENTARY,

BY ANDREW URE, M.D. F.R.S.

*A New Edition,*  
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808.





Some persons imagine, that physical theories are merely systems, to which we wish to accommodate nature, without regard to the practice of the workshops. Yet these theories are themselves only the result of analytical experiments. To observation they always appeal; and, in seeking to direct it, they fix attention on the very facts whose relations cannot as yet be established with those already classed. They indicate, moreover, their application, which they also try to circumscribe within just limits.

The theory of the art of dyeing is connected on one side with the most delicate speculations of natural philosophy; on the other, with the practice of many different arts. It is not to be regarded as a portion of knowledge which can be carried to perfection by itself. Its improvements must follow the advancement of the physical sciences, and of several other arts.

The author of these Elements, whose sole pretensions in this second edition were to render his work less defective, and to introduce recent discoveries, has associated with himself a fellow-labourer,\* who, directing from his youth peculiar attention to this object, may eventually conduct it to greater perfection.

\* This fond parental anticipation does not seem to have been realized. M. Berthollet, junior, died a considerable time before his father.

## TRANSLATOR'S PREFACE.

---

AMONG the academicians of France, who figured in the antiphlogistic revolution of chemistry, M. Berthollet, if not entitled to the first place, yields precedence to Lavoisier alone. His early discovery of the composition of ammonia, was of capital importance. It threw light on many obscure chemical phenomena, and furnished an excellent mirror of gaseous research.

But undoubtedly M. Berthollet's peculiar merit consisted in applying scientific results to the common business of life. Scheele's happy genius, while examining an ore of manganese, revealed to the world that singularly energetic element, chlorine, called by him dephlogisticated marine acid. Amongst its other properties noticed by this distinguished chemist, was the blanching effect it had upon the cork of his phial. This property suggested to Berthollet's active mind a new art, that of bleaching without exposure to sunshine and air. This art, which has been of incalculable benefit to the manufactures of linen and cotton, was expounded by him with much sagacity and address, in a treatise, which forms a principal part of the present publication. Though important improvements in the mode of preparing and applying this blanching power have been made, and particularly by British manufacturers, since Berthollet's time, it must be admitted, that his principles, as far as practice is concerned, have recently received little further elucidation. The theoretical modifications, occasioned by Sir H. Davy's admirable researches on chlorine, with an account of the actual processes adopted by our bleachers, have been briefly stated in the notes of the translator.

M. Berthollet's success in bleaching naturally led the government of France to select him as a fit successor to M. Macquer, in superintending the dyeing establishments of that kingdom. This honourable appointment, previously held by very eminent chemists, turned Berthollet's attention to the art of dyeing, the operations of which he seems to have studied with great assiduity. His Elements of this art must undoubtedly be regarded as constituting the first truly philosophical treatise on the subject; nor has any work appeared since, which can bear a comparison with it for precision of detail and explication. The various essays on dyeing, and dye-stuffs, which have within these few years been multiplied in our Encyclopedias, &c., are, in a great measure, extracts from Berthollet.

It is more than probable, indeed, that these Elements will henceforth be accounted his principal performance; for notwithstanding the air of profound speculation which pervades his CHEMICAL STATICS, and the valuable remarks scattered through that elaborate work, the hypothesis of indefinite combination which forms its basis, has greatly lessened its estimation among chemists, since the theory of definite and multiple combination has been satisfactorily established. Berzelius, in his essay on chemical proportions, has endeavoured, with some ingenuity, to reconcile Berthollet's statical doctrines to the atomic theory, but apparently with little success.

The first edition of the Elements of Dyeing was very ably translated into English by Dr. Hamilton; and had not the French philosopher published a second edition containing important modifications and additions, the labour of the present translator would have been altogether superfluous. It is hoped that the copious notes now appended, will be found a useful supplement to the original work. They contain details of the most remarkable chemical researches connected with dyeing and dye-stuffs which have recently appeared in scientific journals, as also extracts from the valuable work of Vitalis,\* on the Adrianople madder red, and on calico printing, along with some observations not hitherto laid before the public.

The Plates furnished by the translator, represent some of the most useful machines at present employed in our best dyeing establishments.

\* Cours élémentaire de teinture. Paris, 1823.

The following obituary notice of Berthollet was published by M. J. J. Virey, in the *Journal de Pharmacie* for December 1822. It may probably prove acceptable to some readers:—

“ M. Claude-Louis Berthollet, Member of the Royal Academy of Sciences, of the Institute, and of several other academies, Count and Peer of France, &c., was born in 1749, at Talloire, in Savoy. He received the degree of Doctor in Medicine, became attached to the house of Orleans, and entered the Academy of Sciences in 1780. In 1794 he received the appointment of Professor of Chemistry in the Normal school, and subsequently in the Polytechnic school. He was nominated a member of the Institute at its formation. His probity caused him to be appointed to collect the objects of art conquered in our triumphs in Italy. He soon afterwards joined the memorable expedition to Egypt, and returned in 1799, with the extraordinary man who raised him to the rank of senator, along with his colleague, Monge, who appreciated the value of his genius. Nominated to the Chamber of Peers by his Majesty, in 1814, he continued a member of it till his death, which happened on the 6th of November, 1822, at the age of 73 years and a few months.

- “ His splendid career was marked by important discoveries, although his hands were deficient in address, his style and elocution in perspicuity. A friend of the great and unfortunate founder of pneumatic chemistry, Lavoisier, he co-operated with him, with Guyton de Morveau, Fourcroy, &c., in reforming the nomenclature of this science. His analysis of ammonia,—his discoveries on fulminating silver,—the manufacture of the detonating powder of chlorate of potash,—the bleaching of goods by chlorine,—his researches on prussic acid, in which hydrogen acts the (acidifying) part of oxygen,—his valuable labours on dyeing, which first illustrated the principles of this art,—his profound observations on sulphuretted hydrogen, whose acidifying properties he pointed out,—above all, his capital work *Chemical Statics*, of which he had conceived the basis amidst the burning sands of Egypt, and while braving the murderous steel of the Arabs—the foundation of the Chemical Society of Arcueil, in that celebrated retirement of his old age, where he delighted to assemble round him young men eager to collect the fruits of his experience, in order to perpetuate his labours



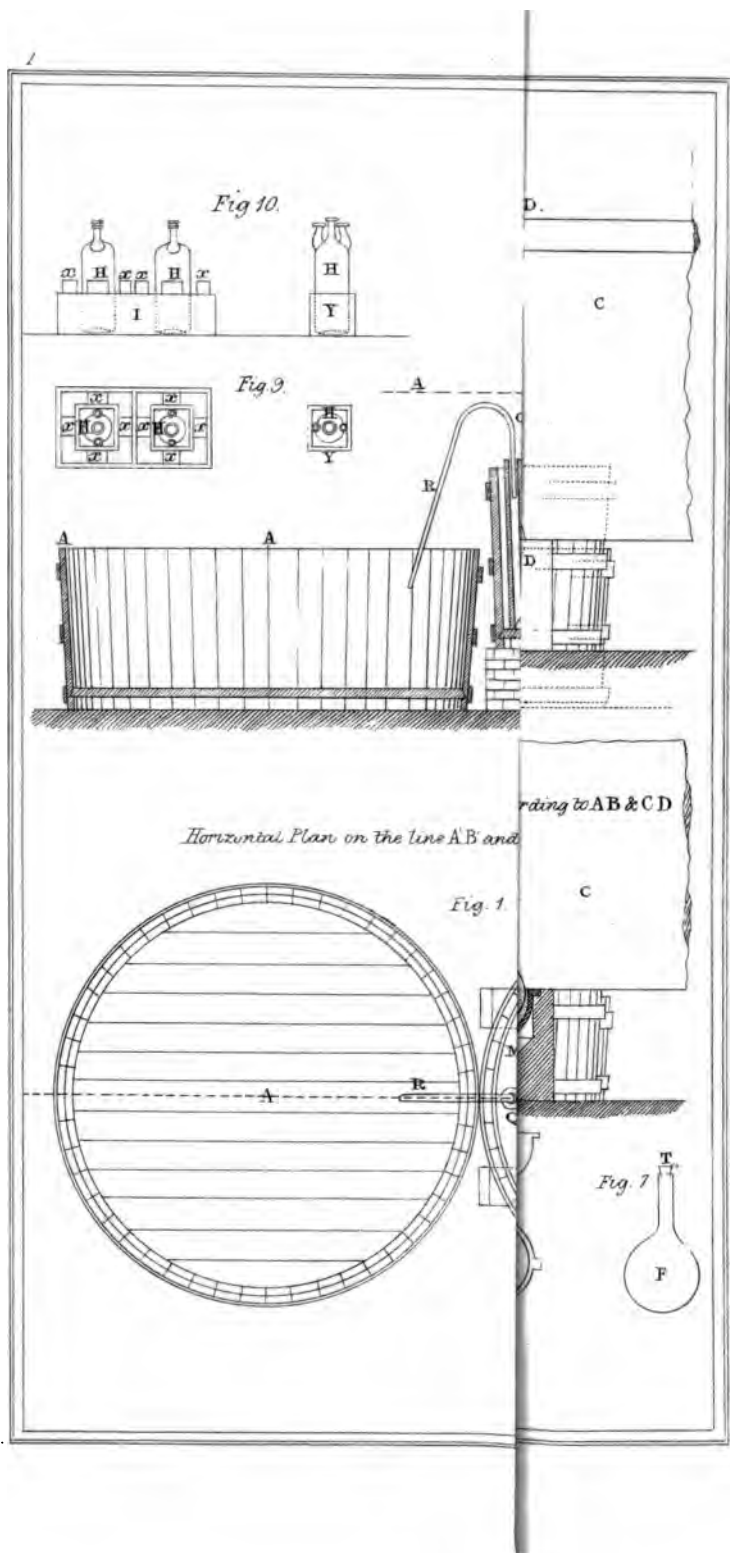
and his renown—such are the titles of Berthollet to immortality, if this award can be at all promised to men.

“If we penetrate into the privacy of his life, we shall see him, under a modest exterior, and a robust frame, concealing a sensible heart; we shall contemplate this soul, too exalted not to be simple in its greatness, possessed of that intrepid firmness, which yielded neither to the accidents of fortune, to dangers, nor to power. Never would his candour make a compromise with error or falsehood, or prefer wealth to self-esteem. Even in the bosom of those political tempests which held nothing sacred, he retained his imperturbable strength of mind. Such lofty virtues were venerated by all parties, zealous to contribute to the illustration of a glory become in some measure European.

“His tomb has received the sincere tears of his friends, Laplace, Chaptal, of his pupils erewhile, but now his honourable competitors, Gay Lussac, Thenard, and many other associates of labours, always subservient to the love of his country and of science.”

GLASGOW, JULY 2, 1824.





## EXPLANATION OF THE PLATES.

### PLATE I. Apparatus for Bleaching by Chlorine.

Fig. 1. Horizontal projection according to the line A'B', and section of the furnaces according to C D.

A, Tub of Immersion.

B, Receiver.

M, M, M, M, M, Plates which close exactly the space between the upper shallow tub, and the sides of the receiver. Only the side looking to the furnace is left open.

Q, Pipe into which the syphon for running the Chlorine solution into the immersion tub is introduced.

O, O, Cross pieces which support the shallow tubs, and are fixed into the extremities N, N, N, N, of four uprights.

K, Circular grooves cut out in the plate, which closes the space between the second shallow tub, and the side of the receiver, for the passage of the conductor tubes, one of which is traced in the figure.

C, C, Partition which separates the receiver from the furnaces.

D, Plan of a furnace, of the boiler E, serving for a sand bath, and of the mattress F, which communicates by the tube G with the intermediate bottle H, enclosed in its double box I: in the furnace, round the sand bath, and opposite each angle, channels have been cut, which serve as chimnies and registers. A section of the second furnace D is made at the height of the fire-place, that the grate *d* may be perceived, and the plate of iron *d'*, which separates the fire-place from the ash-pit.

Fig. 2. Vertical section of the receiver, and of the immersion tub, according to the lines A B and C D.

L, L, L, Shallow tubs, separated from each other by the cross pieces O, fixed on the uprights N. The space between them and the sides of the receiver is closed by the plates M, M, M, so as to leave a free space, but on sides alternately opposite; that is to say, from the side of the furnaces to the inferior shallow tub, as also to the superior, and on the side of the immersion tub, to the middle shallow tub.

P, P, P, Tubes which allow the gas to pass from one shallow tub to its superior, when it contains a stratum of it, equal to the length of these tubes. The tube of the upper shallow tub is made long enough, as is shown, to disperse the gas, which being undissolved in the water, would be diffused in the air, and annoy the workmen.

K, Conductor tube, which proceeds from the intermediate bottle, and terminates under the lower shallow tub.

Q, Pipe which communicates down to the bottom of the apparatus, in order that the syphon R may conduct the most concentrated acid (aqueous chlorine) into the immersion tub.

S, Tube of safety.

D, Elevation of the furnace provided with all its distillatory apparatus.

Fig. 3. Vertical projection of the two distillatory apparatuses, according to the line D D. The letters indicate the same objects as in the two preceding figures.

Fig. 4. Vertical section of a furnace, and of one of the boxes, to show its internal form, and the position of the sand bath.

Fig. 5. Plan of a furnace without a sand bath.

Fig. 6. Plan and elevation of the boiler serving as a sand bath.

Fig. 7. F, mattress; T, cork of the mattress.

Fig. 8. V, small syphon to draw out the air from beneath the shallow tubs.

Fig. 9. I, box, with two square cells, serving to contain the intermediate bottles, drawn on a double scale. Y, small box, which encloses the bottle held in one of the cells, by the corners X, X, X, X.

Fig. 10. Elevation of the same box, furnished with its two bottles.

Plan and elevation of the small boxes, Y.

PLATE II. Fig. 1, 2, 3, 4. Apparatus for the running off leys. The same letters serve for the same objects in these different figures.

Fig. 1. Vertical section of the apparatus.

A, tub.

B, boiler, the bottom of which is concave, and provided with a stopcock T. On the pipe to which this stopcock is attached, a socket is soldered, into which the glass tube, V, enters, that communicates by another kneed socket with one of the wooden pipes F, which afford passage to the steam. This tube serves to show what height the liquor rises to in the boiler. The bottom of this is sustained on the edge of the interior masonry of the furnace, except in the part corresponding to the aperture S, through which the smoke passes off. Its edges are turned back on the masonry for receiving the tub, they are then raised round it, in order that the vapour and the liquid may not find an outlet between the tub and the boiler.

H, Grating of deal, the ribs of which rest at their ends on the edges of the masonry of the furnace, and which are supported by two bars, I I, connected with the grating by four copper straps, which bear upon the corners.

D, Body of the pump. It has at its lower part an inverted cup, pierced with small holes, to prevent in the aspiration (sucking) the introduction of bodies which might hinder the valves from shutting, or might scratch the body of the pump. It is prolonged by a thin copper pipe, C, which, at the upper part of the tub, carries a copper heel, on which the cylinder of copper, K, rests. This cylinder stands on four castors. It carries four sockets, to each of which an arm, X, X, is adjusted, of a length equal to the diameter of the tub, and pierced with holes, like the bulb of a watering pot. In order that the ley raised by the pump may be diffused, the pipe of the pump is perforated in like manner with small holes in the whole portion which corresponds to the copper cylinder; and in order that the ley may not run off by the bottom of this cylinder, it presses exactly at this part on the pipe of the pump. The arms X are fitted on like the bayonet to the muzzle of a musket; they are taken off, for the introduction and removal of the cloths.

The cylinder is terminated by a ratchet wheel L, the number of whose teeth should be a prime number, in order that having no exact divisor, the arms may not be periodically brought back to the same positions. The ratchet L is set in motion by a rod *a*, hooked to one of the pieces of wood that form the frame-work, on which the balance-beam *d* of the pump rests, and fixed very freely by a pin to a horizontal rod *b*. This rod is fixed in like manner, by its other extremity, to one of the branches of a bell movement M, whose other branch communicates, by the rod *c*, with the balance-beam. Hence, on turning the handle *e*, every movement of the balance-beam is communicated to the rods, and onwards to the ratchet, which, for each stroke of the piston, percurs the space of one tooth.

The body of the pump D and the pipe C, are joined by two straps and screws. Under these straps passes an iron collar, traversed by six bolts, whose screwed ends are fixed with nuts to a copper platform placed on the grating, and bears no weight on the bottom of the boiler. The pipe C is also held fast at its upper end by an iron strap, adapted to, and fixed on the cross bar *f*.

G represents the copper funnel, by which are introduced the solution of potash, and the waters necessary for the lixivium. It terminates in one of the tubes F, to prevent the solution of potash spouting out on the adjoining pieces.

P indicates the form of the fire-place, the grate being at R, and the ash-pit at Q. The smoke issues by the aperture S, of which only half the altitude is seen here; it circulates by the flue U round the boiler, entering then into the tube of the chimney, which rises vertically.

Fig. 2. Horizontal section of the tub taken above the platform of copper *l*, on which are fixed by nuts the six bolts which support the body of the pump.

*m*, Furnace door.

The dotted lines *nn*, indicate the separation, formed by fire bricks, in the flue which runs round the boiler, and which determines the entrance of the smoke into this passage, as well as its issue into the vertical pipe *p*.

Fig. 3. Vertical projection of the apparatus taken in another direction.

*h*, Register, with which the chimney *p* ought to be furnished.

*g*, Rim of the boiler turned up on the outside of the tub.

Fig. 4. Horizontal projection of the apparatus, according to the line T' G'.

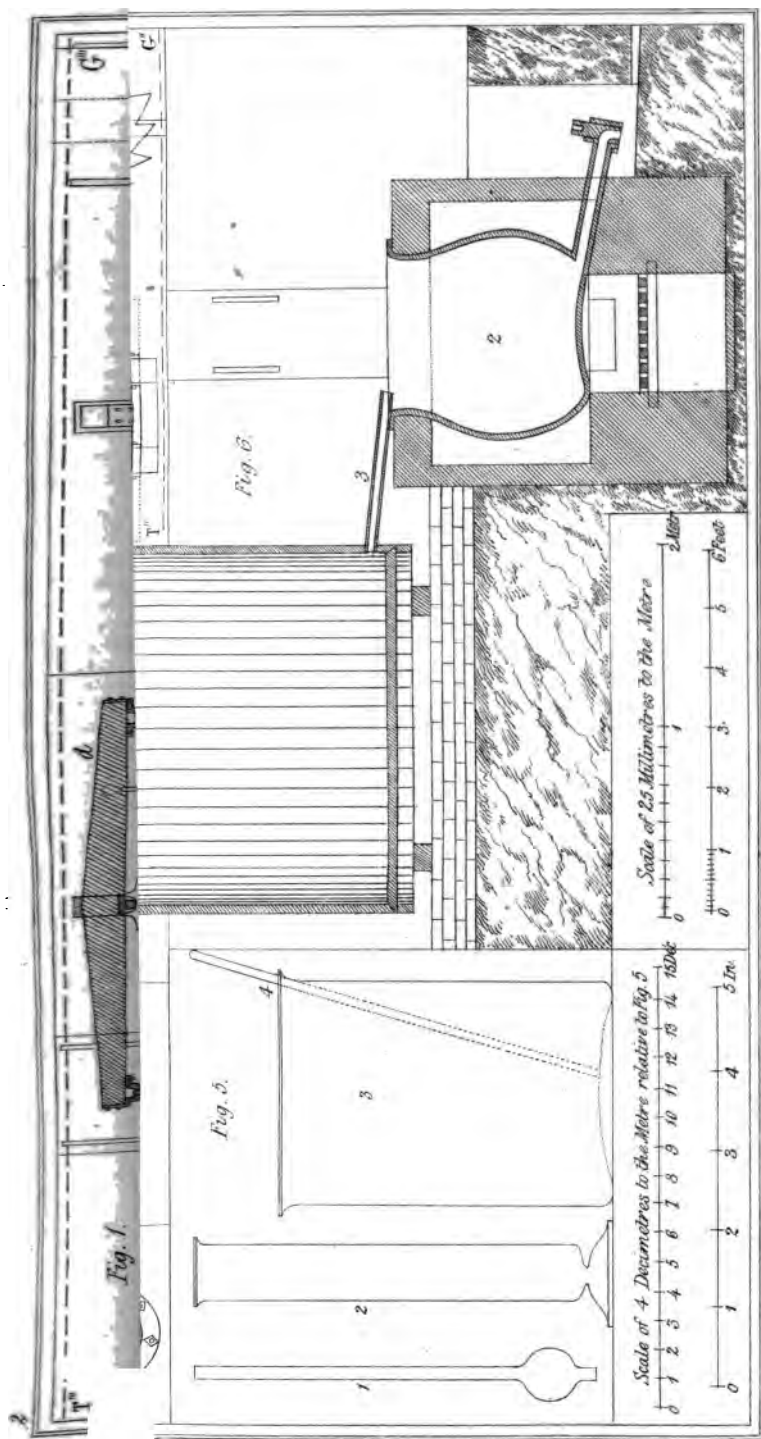




Fig. 2. V, Horizontal projection of the body of the pump, in which the details of the adjustment of the piston are represented.

D, Vertical section of the body of the pump; *r*, clack valve. *s*, piston; *t*, cup attached by a strap to the lower extremity of the body of the pump.

Fig. 4. Horizontal projection, and vertical section of the cylinder K, which bears the sockets to which the arms X X are adjusted.

C, copper pipe to which is soldered the heel *x*: *y*, *y*, brass castors which rest on the heel *x*, and which support the cylinder K.

*u*, *u*, *u*, sockets having an opening for receiving the knob soldered to the extremity of the arms. L, ratchet wheel fixed to the upper part of the cylinder K. It contains in the figure 17 teeth.

These two figures have been made on a double scale, in order that the details might be better understood.

The apparatus for chlorine, and for the running off of leys, are on the same scale.

N.B.—To avoid embarrassing the figures, a small plank is not represented here, which, when the apparatus is constructed on as large dimensions as at present, should be placed at about two yards from the ground, for throwing the goods upon, and from which a child can hand them to the workman, who arranges them in the tub.

Fig. 5. Vessels for the testing of potashes.

1. Small measure; it is filled by plunging the bulb into the liquid, and stopping the tube with the finger whenever it is full. It may then be carried without fear of losing what it contains. To make it flow, the finger has only to be lifted.

2. Tube containing up to the mark 50 times the small measure.

3. Goblet or jar in which the mixture of the test acid is made and the solution of potash.

4. Tube employed for stirring, and making the traces on stained paper.

For the trial of chlorine, the small measure is filled with the solution of indigo, which is poured into a glass jar of the same form as the above, or into a glass tumbler; then the number of measures is introduced that are required for discharging its colour.

Fig. 6. Ordinary distribution (arrangement) of the mode of running off leys.

1. Tub on whose bottom a wooden grating is placed, or some simple pieces of wood, which prevent the cloths, when heaped, from choking up the aperture of the pipe 3, by which the ley falls back into the boiler.

2. Boiler, here represented cut vertically through its diameter, or order to see its form. Those usually employed are different, and do not possess the advantage which the present one does, of directing the liquid, which spouts up, when the ebullition is brisk, towards the middle of the boiler. It has been, moreover, represented as mounted on a furnace different from those which the bleachers usually construct. Its construction is nearly the same as that of the furnace of

Fig. 1. The form of this boiler and of its furnace is adopted in a great many dye-houses. When their dimensions are good, there is much economy of fuel, and convenience of manipulation. Those of the figure have been copied from well constructed furnaces. If pit coal be burned, the height of the fire-place should be diminished a little, and if turf, a little increased.

Instead of sinking the furnace into the ground, its bottom may, however, be put nearly on a level with that of the tub, and the ley made to fall back from the tub into the boiler by a kneed pipe, which reaching to near the bottom of the tub, and opening above the boiler, does the office of a syphon, and reconveys to it the leys which had gone through the whole thickness of the goods.



## EXPLANATION OF THE PLATES

FURNISHED BY THE TRANSLATOR.

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PLATES I. and II. represent the padding machine, for applying mordants to cotton cloth, or generally speaking, for passing cloth through any chemical solution. It consists of a frame in which are placed two rollers, either of wood with an axis of iron, or of cast-iron covered with copper. The upper roller is pressed, by means of levers, against the under one, which revolves horizontally in a box, containing the mordant that is to be put on the cloth.

The bevelled wheel and shaft that convey the power to the padding machine, are represented in plate II. as inclined; a circumstance not essential, but accidentally required in the particular machine from which this drawing was taken.

Plates III. and IV. represent the wash or dash wheel. The pieces of cloth are put into the quadrantal compartments of the wheel, into which a stream of pure water flows through a circular slit in its posterior surface. By the rotation of the wheel, the cloth is dashed backwards and forwards between the quadrantal partitions. Twenty-five revolutions per minute is the proper speed of a wash wheel six feet in diameter. Some persons suppose them to perform better with twenty-six or twenty-seven revolutions; but any considerable deviation from this velocity either impairs the utility of the machine, or destroys its functions altogether. In these and the other plates, the parts are so distinctly delineated by the artist, as to supersede the necessity of letters of reference and minute explanation.

Plate V. A bucking boiler, exhibiting the fire-place, the iron boiler, surmounted by the wooden crib, with its grated bottom and central iron pipe. Whenever the water or alkaline ley boils briskly, its vapour, confined by the goods in the crib, presses on the surface of the liquid, and forces this to issue in a sudden stream from the top of the pipe, whence it is spread over the surface of the goods, and gradually percolates down through them. The liquid in its descent becomes slightly cooled; but after a little while, accumulating and becoming hot again in the boiler, a new eruption of boiling liquid takes place. A more complex, though, I believe, not a more effective form of bucking apparatus, is described in the *Edinburgh Encyclopedia*, article *Bleaching*.

Plates VI. and VII. Cylinder printing machine.

A. The engraved copper roller.

B. The mandril on which the roller is fixed.

C. The back roller covered with soft materials. It presses the piece of cloth to be printed against the copper roller.

D. Situation for a second copper roller, when two colours are to be applied at once. In this case, the back roller is pressed against it by means of the screws E.

F. The colour-box.

G. Steel doctor for scraping off the colours from those parts of the roller which are not engraved.

H. Wheel which gives a horizontal motion to the doctor.

I. A long piece of thick woollen cloth, sewed end to end, which passes under the back roller, along with the piece of cloth to be printed.

K. Beam on which the pieces of cloth are rolled before being printed.

# C O N T E N T S.

Historical Summary of the Art of Dyeing . . . . .	Page 1
---	-----------

## FIRST PART.

### OF DYEING IN GENERAL.

#### SECTION I.

##### OF THE GENERAL PROPERTIES OF COLOURING SUBSTANCES.

CHAP. I. Of the Theory of Colours, and of the distinctive Properties of Colouring Particles . . . . .	19
II. Of Mordants . . . . .	40
III. Of Astringents in general, and particularly of the Gallic Acid and Tannin . . . . .	53
IV. Of the action of different substances, particularly of Air and Light, on Colours . . . . .	71
V. Recapitulation of the Theory laid down in this Section . . . . .	87

#### SECTION II.

##### OF THE DIFFERENCES WHICH DISTINGUISH WOOL, SILK, COTTON, AND LINEN, (FLAX,) AND OF THE OPERATIONS BY WHICH THESE SUBSTANCES ARE DISPOSED TO RECEIVE DYES.

CHAP. I. Considerations on the differences between Animal and Vegetable Substances . . . . .	93
II. Of Wool . . . . .	95
III. Of Silk . . . . .	101
IV. Of Cotton . . . . .	108
V. Of Flax and Hemp . . . . .	111

#### SECTION III.

##### OF BLEACHING BY THE OXYGENATED MURIATIC ACID (CHLORINE.)

Introduction . . . . .	116
CHAP. I. Theory of Bleaching . . . . .	118

	Page
CHAP. II. Of the Preparation of Chlorine Liquor . . . . .	121
III. Of Leys . . . . .	126
IV. Of the Immersions in the Chlorine Liquor . . . . .	136
V. Of the Washings . . . . .	139
VI. Of the other Operations of Bleaching . . . . .	141
VII. Number and Order of the Operations . . . . .	144
VIII. Of the different Preparations of Bleaching Liquor . . . . .	146
IX. Of the other Uses of Chlorine . . . . .	150
1. Preliminary Maceration of the Fibres . . . . .	158
2. Of the Leys and Immersions in Chlorine . . . . .	159
3. Bath of Sulphuric Acid . . . . .	160
4. Soaping . . . . .	ib.
5. To give Pliancy to Hemp-Cotton . . . . .	161
6. To give the Appearance of ordinary Cotton to Hemp-Cotton . . . . .	ib.

## SECTION IV.

## OF DYEING OPERATIONS IN GENERAL.

CHAP. I. Of Dye-houses and the Manipulations of the Art of Dyeing . . . . .	162
II. Of Fuel . . . . .	166
III. Of the Means of ascertaining the Goodness of a Colour (Dye) . . . . .	174
Instructions concerning the Debouilli (chemical trials) on Wool and Woollen Cloths . . . . .	179

## SECTION V.

## OF THE CHEMICAL AGENTS EMPLOYED IN DYEING.

CHAP. I. Of the Acids . . . . .	188
1. Of Sulphuric Acid . . . . .	191
2. Of Nitric or Nitrous Acid . . . . .	194
3. Of Muriatic Acid . . . . .	200
4. Of Aqua Regia, or Nitro-muriatic Acid . . . . .	205
5. Of Bitartrate and Binolate of Potash, and of Acetic Acid . . . . .	210
II. Of Alum, or the Sulphate of Alumina . . . . .	215
III. Of the Sulphate, and some other Combinations of Iron . . . . .	224
IV. Of Sulphate of Copper . . . . .	229
V. Of Verdigris, or the Acetate of Copper . . . . .	231
VI. Of the Acetate of Lead, or Salt of Saturn . . . . .	235
VII. Of the Fixed Alkalies . . . . .	237
1. Of Potash . . . . .	ib.
2. Of Soda . . . . .	242
VIII. Of Soap . . . . .	245
IX. Of Sulphur . . . . .	248
X. Of Waters . . . . .	250

## SECOND PART.

### OF THE PROCESSES OF ART.

#### SECTION I.

##### OF BLACK.

	Page
CHAP. I. Of the Processes for Dyeing Black . . . . .	253
II. Observations on the Processes for Dyeing Black . . . . .	265
III. Of Grey . . . . .	269

#### SECTION II.

##### OF BLUE.

CHAP. I. Of Indigo . . . . .	273
II. Of Pastel and Woad . . . . .	286
III. Of Dyeing Blue with Indigo and Pastel Vat . . . . .	290
IV. Of Saxon Blue . . . . .	303
V. Of Dyeing Blue by means of Prussiate of Iron . . . . .	307

#### SECTION III.

##### OF RED.

CHAP. I. Of Madder . . . . .	313
II. Of the Processes used in Dyeing with Madder . . . . .	320
Process of Adrianople, or Turkey Red . . . . .	327
III. Of Cochineal . . . . .	342
IV. Of Dyeing Scarlet . . . . .	347
V. Of the Crimson Dye . . . . .	354
VI. Of Kermes . . . . .	359
VII. Of Lac, or Gum Lac . . . . .	363
VIII. Of Archil . . . . .	365
IX. Of Carthamus . . . . .	369
X. Of Brazil Wood . . . . .	377
XI. Of Logwood . . . . .	384

#### SECTION IV.

##### OF YELLOW.

CHAP. I. Of Weld . . . . .	388
II. Of Fustic ( <i>Bois Jaune</i> ) . . . . .	393
III. Of Quercitron . . . . .	395
IV. Of Annotto ( <i>Roucou</i> ) . . . . .	398
V. Of Saw-wort ( <i>Sarrette</i> ) <i>Serratula Tinctoria</i> , and several other Articles capable of Dyeing Yellow . . . . .	402

## SECTION V.

## OF DUN, ROOF, OR FAWN COLOUR (FAUVE.)

	Page
CHAP. I. Of Walnut Peels . . . . .	409
II. Of Sumach, and some other Substances capable of affording a Dun Colour . . . . .	412

## SECTION VI.

## OF COMPOUND COLOURS.

CHAP. I. Of the Mixture of Blue and Yellow, or Green . . . . .	419
II. Of the Mixture of Red and Blue . . . . .	428
III. Of the Mixture of Red and Yellow . . . . .	438
IV. Of the Colours resulting from the Mixture of Black with other Colours, and of Brownings . . . . .	440



JAT

# HISTORICAL SUMMARY

OF

## THE ART OF DYEING.

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THE desire of attracting public admiration may be observed even in the least civilized state of society. Among the means of distinction which are eagerly laid hold of, the glare of colours is one of the most obvious. Savages assume an imposing aspect, by staining their skins, or wearing feathers, stones, and shells, with gaudy colours. The Gaulish women gave themselves, on festivals, an olive-brown complexion, by means of woad ; and those of high rank were no doubt jealous of this distinction.

The art of dyeing, therefore, has unquestionably a very ancient origin ; for when nature afforded colouring substances of easy application, there might arise among people but slightly civilized, methods of dyeing which have been sought after by polished nations. Thus the Gauls prepared some dyes which were not disdained by the Romans. But for its enlargement and perfection, the art required to follow the progress of manufactures and luxury.

The Egyptians, according to Pliny,\* had discovered a mode of dyeing analogous to that of our printed calicoes. Cloths, impregnated probably with different mordants, were plunged in a bath, in which they assumed different colours. He alludes to the employment of these mordants in the following passage : *Candida vela postquam attrivere, illinuntur non coloribus, sed colorem sorbentibus medicamentis.* It may, however, be presumed, that manufactures possessed little activity among a people

\* Hist. Natur. lib. xxxv. cap. 2.

where the authority of the priesthood prohibited by law every change in even the most indifferent customs.

It is to Greece that our attention turns, when we wish to ascertain the progress which the human mind had made in antiquity. Here, however, we find a vast difference between the fine arts,\* and the useful arts, or the arts of luxury; a difference of which the cause is obvious. Public opinion set these arts at an immense distance from each other: glory was associated with the former, but the latter were confounded with servile labours.

This distinction was, in some measure, well founded. The painter, the statuary, the architect, stamped their genius on their productions. Their arts did not each require a long series of efforts for its advancement; nor did it enrich itself slowly by the casualties and experiments of ages. Imagination could suddenly overleap the boundaries of time; and the masterpieces which appeared in rapid succession among the Greeks were destined to become the admiration of posterity.

Yet this people, so ingenious, so sensitive, and so fertile in great men, suffered themselves to be seduced in the distribution of their esteem by tastes often frivolous. He who won a victory in wrestling, pugilism, or the race, obtained crowns, and enjoyed the greatest honours; but the useful arts were degraded even in the eyes of their philosophers.

Here we perceive one of the most striking characters which distinguish the ancients from the moderns. The Greek philosophers, occupied especially in speculations which might ensure to them the homage of a people so prone to enthusiasm, regarded the useful arts as unworthy of their attention. This contempt was inherited by the Romans. Pliny, in speaking of dyeing, avowedly neglects to describe operations which do not belong to a liberal art. *Nec tingendi rationem omissemus, si unquam ea liberalium artium fuisset.*

Ever since philosophy has taken observation for a guide, and, abandoning the illusions of systems, has adhered to the study of the phenomena of nature, and of the real properties to which they owe their origin, it has followed the chain of the numerous wonders which it has analyzed, in subserviency to the welfare

\* Poetical arts would be here a juster expression; for statuary is surely an art of luxury.—T.



of society. It has recognized in manufacturing industry, as well as in commerce, the source of the prosperity of the nation, the germ of a great population, the principal support of agriculture. But it was the Academy of Sciences of Paris which first sought to spread the light of science over all the arts, which first formed the project of publishing their description, and which, in the midst of prohibitory ordinances, arrived at this truth,—That national industry was to be augmented and enlightened by a free communication of the processes which it employed; and that the sacrifices which it might make by this publicity, are well recompensed by the advantages thence derived. This project was extended to all the objects of our studies, by the *Encyclopædia*, the mightiest monument which philosophy and reason have ever raised.

The art of dyeing must have felt feebly, we perceive, the influence of learning among the Greeks. Yet the activity of genius has something sympathetic, and industry multiplies her trials when solicited by luxury. Let us observe, then, to what point refinement had raised it in the prosperous days of Greece; let us consult the picture of it traced by Barthelemy.

“A great proportion of the citizens of Athens passed their time in the different tribunals, and received a salary of three oboli, that is, fourpence halfpenny a-day. The average price of the *setier* (twelve bushels of Paris) of corn, whose value is the least uncertain standard of comparison, was thirteen French livres, (10s. 10d. English), that is, a little more than the half of the medium price with us. A citizen of Athens could thus, with the daily pay annexed to the most important functions of the republic, purchase a measure of corn, which would at present cost sevenpence halfpenny English. In order to form an idea, therefore, not indeed of the public magnificence, nor of that of some individuals, but of the ease and luxury of the ordinary class of citizens, we must represent to ourselves what they would be at Paris, if the salary of the public functionaries was fifteen *sous* (sevenpence halfpenny) a-day.

“Many of them (the Athenians) went barefooted. The common people were clad in cloth which had received no dye, and which could therefore be re-whitened. The rich preferred coloured clothes :\* they held in considerable estimation those

\* Voyage de jeune Anacharsis.

which had been dyed scarlet, by means of small reddish grains, and in still higher those of a purple dye."

Silk, which is subjected to the most varied processes of dyeing, comes originally from China. It was, say the Chinese annals, the wife of the emperor Hoang-ti who first engaged in spinning the cocoons which are naturally found on trees. Silk was carried thereafter into Hindostan, and thence into Persia, Greece, and Rome. But it arrived here at a very late period. Some have concluded, from a verse in the Georgics of Virgil,\* that its use was known at Rome in the time of Augustus. We find less doubtful indications in Pliny. Silk bore still so high a price in the time of the emperor Justinian, that it was sold for its weight of gold.† Lastly, some monks brought from India to Constantinople eggs of the silk-worm, and established there the method of rearing them, and of spinning the down of their cocoons.‡

It appears to have been in the time of the Crusades that silk-worms were introduced into Italy.

The art of dyeing webs seems to have been unknown in Greece before Alexander's invasion of India. Pliny relates, that the sails of his vessels were there dyed of different colours. Hence the Greeks possibly borrowed this art from the Indians.

India is indeed the nursery of that knowledge and those arts which were subsequently diffused and improved among other nations. Fortunate accidents might be readily multiplied in a country rich in natural productions; which requires little labour to supply the subsistence of its inhabitants; and whose population was promoted by the profusion of nature, and the simplicity of manners, ere the tyranny of those conquerors who have now succeeded to it had committed its ravages; but religious prejudices, and the unalterable division of castes, soon shackled industry. The arts have been thenceforward stationary in India: and it would appear, that in the time of Alexander, dyeing had attained nearly the same state as at present, in regard to cotton goods; for silk was still unknown there, or at least very scarce.

The beautiful colours which we observe on the Indian goods,

\* *Velleraque ut foliis depectant tenuia Seres*.—Georg. lib. ii.

† Voltaire, *Essai sur les Mœurs*, &c.

‡ Procop. lib. iv. cap. 17. *De bello Gothico*.

to which the name of *Perses* was originally given, because it was through the trade of Persia that they first reached us, might lead to the belief that the art of dyeing was there pushed to a great degree of perfection. But we learn from the description which Beaulieu gave, at the request of Dufay, of operations performed in his presence,\* that the processes of the Indians are so complicated, tedious, and imperfect, that they would be impracticable elsewhere, from the difference in the price of labour. European manufactures soon surpassed them in correctness of design, variety of shade, and simplicity of manipulation. If they have not yet rivalled the vivacity of two or three of their colours, this must be ascribed merely to the superiority of some colouring substances, or perhaps to the very length and multiplicity of the operations.

We may therefore conclude, that the art of dyeing was less extended and less improved among the ancients than among the moderns; but the former possessed a dye which has been lost or neglected, and which was the most eagerly desired object of luxury,—this was purple. Its processes have, however, been better preserved in historical monuments, than those of any other colours.

We shall not dwell on the tales with which it has been attempted to embellish the origin of the purple dye. There is a great probability of the discovery having been made at Tyre, and that it contributed much to the opulence of this celebrated city.

The liquor which was employed to dye the purple, was derived from two principal species of shells. The larger bore the name of the *purple*; and the other was a species of whelk. Both were subdivided into several varieties. They were further distinguished by the greater or less beauty of colour which they could afford, and according to the coasts where the fishing was carried on.

The colouring juice of the *purples* is contained in a vessel which is found in the throat. Only one drop of liquid was obtained from each shell-fish. The whelks were bruised: These contained a very small quantity of a red liquor, verging on black. (*Nigricantis Rosæ*.—PLIN.)

\* "Traité sur les toiles peintes," in which we observe the manner of fabricating printed calicoes in India and in Europe. The opinion given in the text is confirmed by the more exact detail found in Bancroft "on Permanent Colours."

When they had collected a certain quantity of the colouring liquor, they added to it a proportion of sea-salt. They then macerated for three days; after which five times as much water was added. This mixture was kept at a moderate heat, separating from time to time the animal matters which rose to the surface. These operations lasted ten days. They now tried, with a little white wool, if the liquid had taken the proper hue. The stuff was subjected to different preparations before it was dyed. Some passed it through lime-water; others prepared it with a species of *fucus*, which served, like some of our astringents, to render the colour more durable. We do not know precisely the marine plant to which the ancients gave the name of *fucus*; but it was of such extensive use in their dye-works, that the word became a generic name for all kinds of colouring substances, (dye-stuffs.) Pileur d'Apligny conjectures, that it might be a species of *archil* or *rocella*, which is found on the coasts of Candia;\* others, again, prepared the cloth with alkanet.

The juice of the whelk did not yield of itself a permanent colour; but it increased the brilliancy of the colour of the other shell-fish. The purple of Tyre was made in two operations. They commenced by dyeing with the juice of the *purpura*; after this they gave it a second dye with the juice of the whelk, whence Pliny calls it *purpura dibapha*. In other processes, the liquors of two species of shell-fish were mingled; thus, for 110 pounds of wool, 440 pounds of the liquor of the whelk, and 220 pounds of that of the *purpura* were taken. An amethyst colour was thereby obtained. Sometimes a body or basis was given with the *coccus*, which is our *hermes*, and after that the dye was completed with the juice of the *purpura*. Finally, they combined some of the preceding methods, and thereby obtained a great variety of purple hues, which were distinguished by different names. That of Tyre possessed, according to Pliny, the colour of coagulated blood; the amethyst purple had that of the stone so called; another species resembled violet, &c.†

\* *Essai sur les moyens de perfectionner l'art de la teinture.*

† Those who wish to acquire more extensive information on the purple of the ancients may consult among the moderns the following works:—"Fabii Colomni lyncei purpura;" "G. Gottl. Richter, Progr. de purpuræ antiquo et novo pigmento;" "Reaumur, Mem. de l'academie, 1711;" and especially a learned work by M. Bischoff, entitled, "Versuche einer Geschichte der Faberkunst, &c. 1788."

It seems that some kinds of purple preserved their colour a very long time : Plutarch relates, in the life of Alexander, that the Greeks found in the treasury of the king of Persia a great quantity of purple, of which the beauty was not affected though it was 190 years old.

The very small quantity of liquor which was extracted from each shell, and the length of the dyeing process, gave to the purple so high a price, that, in the time of Augustus, a pound of wool dyed in Tyrian purple could not be had for less than 1000 *denarii*, about 700 French livres, (£28 sterling.)

The priests, who sought always to take advantage of what might make an impression on the people, attributed, in early times, a sacred character to the purple. It was a colour pleasing to the Deity, and which must be reserved for his worship. Although the purple has been lost for a long time, the pride of the name has been preserved in our sacerdotal hierarchy.

Purple was almost every where an attribute of exalted birth, and of dignities. It served as a decoration to the first magistrates of Rome. But the luxury which was afterwards carried to excess in this capital of the world, rendered the use of it common to opulent individuals, until the emperors reserved to themselves the privilege of wearing it. It soon became the symbol of their inauguration. They appointed officers who were charged with the superintendence of this dye in the manufactories, where it was prepared for them alone, principally in Phœnicia. The punishment of death was decreed against all those who might have the audacity to wear purple, even should they cover it with another dye.

The penalty annexed to this whimsical kind of high treason, was undoubtedly the cause which made the art of dyeing purple disappear, first in the West, and much later in the East, where this art still existed in vigour in the eleventh century.

There was extracted from *coccus*, now known under the name of *kermes*, (an account of which may be seen Sect. iii. Part 2,) a dye, which was hardly less esteemed than the purple, and which was sometimes associated with it, as we have already mentioned. Pliny relates, that it was employed for the robes of emperors. The name of scarlet was usually given to it; but it was sometimes confounded with purple.

It was only in the age of Alexander and his successors,

according to Pliny, that the Greeks sought to give some perfection to black, blue, yellow, and green (dyes.)

Among the Romans, newly married women wore in the early times a yellow veil. This colour was appropriated to matrons.

In the games of the circus, four parties were distinguished by their colours: green, *color prasinus*; orange, *rufatus*; ash-colour, *venetus*; and white.

We may judge of the qualities of these colours by the substances which they employed. As Bischoff has made very extensive researches on this subject, I shall give, after him, an enumeration of the ingredients which entered into the art of dyeing in those times, independently of the *coccus* and the purple shell-fish.

1. Alum; but we may see in the first part of this work, (Sect. v.) that very probably the ancients were not acquainted with our alum in a state of purity.

2. Alkanet. Suidas relates, that the substance served likewise as a pigment for women.

3. The blood of birds, which was employed by the Jews.

4. The fucus. That of Crete was preferred. It was usually employed to give a basis or ground to good colours.

5. Broom.

6. Violet. The Gauls prepared from it a colour which resembled one species of purple.

7. Lotus medicago arborea. Snail trefoil, (Luzerne en arbre.) The bark served for dyeing skins, and the root was employed in dyeing wool.

8. The bark of the walnut tree and the rind of the nut.

9. Madder. It is not known whether the madder of the ancients be the same plant as ours, or some other root of the same family.

10. Woad. (*Glastum*.) This plant was certainly employed by the ancients; but it is doubtful if they gave it the same preparation as we do.

They made use of the sulphate of iron, and of that of copper, for dyeing black, especially skins. Nut-galls, of which the most valued came from Comagena, served as the astringent. They used, as a substitute for it, the seeds contained in the pods of an acacia peculiar to Egypt. They also employed the bark of pomegranate and of some other astringents.\*

\* Ameilhon, Mém. de l'Institut. littér. et beaux arts, tom. iii.

Although the ancients may have used some substances of which no memorial is preserved, it is easy to see that the acquisitions which we have made, especially since the discovery of America, give us a great superiority with regard to several colours. But is the regret frequently expressed for the loss of the purple well founded? Are we not able to rival the beauty of this highly-famed colour?

The shell-fish which furnished the colouring liquor of the purple, exist probably in as great abundance as formerly. They have been sufficiently characterized to enable us to recognize them. In fact, Thomas Gage relates that there was found near Nicoya, a small Spanish town of South America, shell-fish possessed of all the properties described by Pliny and the other ancient writers. It appears, even, that some use was made of these shell-fish for dyeing cotton on the coasts of Guayaquil and Guatemala.\* Cole discovered some of them in 1686 on the English coasts; Plumier found a species of them at the Antilles; Reaumur made several experiments on the *buccinum* which he found on the coasts of Peru; Duhamel made also several on the colouring juice of the shell-fish which bears the name of *purpura*, which he found in abundance on the coasts of Provence. He observed that this juice assumes a purple colour only by the action of light, as Reaumur had already remarked respecting the colouring juice of the *buccinum*; that this juice, at first white, assumes a yellowish-green colour, which deepens, verging on blue; that, finally, it is seen to redden, and in less than five minutes to become of a very vivid deep purple colour.† Now, the purple of the ancients possessed these characters.

Moreover, we have a very detailed description of the manner in which the fishing was conducted of the shell-fish which served for purple, in a work of an eye-witness, Eudocia Macrembolitissa, daughter of the emperor Constantine VIII., who lived in the eleventh century.‡

Our indifference, therefore, in procuring the purple, and in

\* Histoire philosophique et politique du commerce des Indes, liv. viii.

† Mem. de l'Acad. 1736.

‡ Eudocia Macrembolitissa was married to a Constantine, and after his death to Romanus III., who was elected emperor in 1068. Her work is to be found in a collection published by M. d'Anse de Villosion, under the title of "Anecdota Græca à regiâ parisiensi et à venetâ S. Marci bibliothecis deprompta, T. i. 1781."

profiting by the researches which some moderns have successfully made, probably proceeds from our having acquired more beautiful and less costly colours. Many learned men are of this opinion.\*

In fact, the kermes afforded a colour which was esteemed by the ancients as almost equal to the *purple* (purpura,) and which contributed to that distinguished by the name of *color hysginus*. Now, we understand the management of the kermes in probably a more advantageous manner than the ancients did, because we possess a pure alum, which disposes the stuff to receive a finer and more permanent colour; and yet our dyers have been obliged to renounce its use almost entirely, notwithstanding the solidity of its colour, because it cannot, in point of beauty, bear a comparison with the colours now produced from cochineal.

Supposing the slight difference which may exist between the colour of the kermes, and that of the purple of Tyre, to be compensated by the advantage which we derive from our alum, we might regard this purple, which was so precious that the Cæsars reserved it to themselves under penalty of death, to be similar to that blood-red which we observe in ancient tapestries, for the production of which kermes was employed.

The supposition, that the colour which we derive from kermes is preferable to that which the ancients obtained from it can be supported by the testimony even of Pliny; for he insinuates that it had little permanence; but the colour which is now given by means of kermes, to wool prepared with alum, is of the greatest durability.

Soap, the discovery of which is ascribed to the Gauls, appears to have had no other use among the ancients than that of a pomade for cleansing the hair, or for staining it with any colours which they chose to mix with it.† This substance is, however, of such utility, that it must give us a superiority in bleaching, and in some parts of dyeing. They supplied its use, in the scouring of wool and whitening of cloth, by a plant which Pliny calls *radicula*, which was termed *struthion* by the Greeks, and which some consider as our *saponaria*; as also by another plant, which Pliny designates as a species of poppy. Homer

\* Bischoff, Versuche, &c. Gognet, de l'origine des lois, arts, et des sciences, 2 partie, liv. ii.

† Gognet, Ibid. première partie, liv. ii. Ameilhon, Mém. de l'Institut. tom. ii.



paints the princess Nausica and her waiting-maids treading their dresses with their feet in ditches in order to bleach them. From other evidence we learn that wood ashes were mingled with them; and also, that some earthy boles were employed.

We have acquired from the New World several dye-stuffs, cochineal, Brazil wood, logwood, annotta. We owe the superiority of our dyes especially to the preparation of alum and to the solution of tin, which lends such lustre to several colouring substances. Silk, which has become so common with us, and which takes such lively and brilliant dyes; the rapid movements of commerce, which place the productions of China and the Indies within the enjoyment of even the common people; an active and enlightened industry, stimulated by the rivalry of the different nations of Europe, who endeavour to counterbalance their instruments of power; all these circumstances set an immense interval between the luxuries most familiar to us, and those of the most opulent individuals among the ancients. Europe, however, before acquiring this superiority, experienced all the devastations of barbarism.

In the fifth century the arts became extinct in the West; soon thereafter, almost every trace of intelligence, reason, humanity, and industry, disappeared. A few decayed arts, indeed, were preserved merely in Italy. Muratori quotes a manuscript of the eighth century,\* in which we find some description of dyes, chiefly for skins, and some processes of the other arts; but the Latin, which is almost unintelligible, and some chasms in the writing, prevent us from forming a just idea of these processes.†

The arts were better preserved in the East, whence were derived, till the twelfth century, the objects of luxury which a few of the great were able to procure. During the Crusades, the Venetians reared their power on the frenzy of the age: their fleets took charge of the victualling of our fatal emigrations; their commerce became enriched; the arts were established among them, enlightened by the manufactures of the Greeks; and from this city they were propagated into the other parts

\* Diss. de texturis et vestibus sæculor. rudium antiq. ital. vol. ii.

† I shall quote literally a description of alum, which seems to prove, that only aluminous stalactites, or a volcanic earth impregnated with alum, was used. "DE ALUMEN. ALUMEN autem metallum, est terra floriens de eritarin. Eritarin terra est alba, facilis ad pisandum."

of Italy. In 1338, 200 manufacturers were employed in Florence, who fabricated, it was said, from 70,000 to 80,000 pieces of cloth, forming an object of commerce worth 1,200,000 golden crowns.

The discovery of *rocella* was accidentally made by a merchant of Florence, about the year 1300. Having remarked that urine gave a fine colour to a species of moss, he made experiments, and learned to prepare *archil*. He kept this discovery secret for a long time. His descendants, of whom a branch still remains, according to the report of Dominique Manni, have retained the name of *Ruccelai*, from the Spanish word *oreiglia*, which that species of moss bore.

The arts long continued to be cultivated in Italy with increasing success. In 1429 appeared at Venice the first collection of processes employed in dyeing, under the name of *Mariegola dell' Arte de Tentori*. A second edition of it, much enlarged, was given in 1510. One *Giovan Ventura Rosetti* formed the project of giving more extent and utility to this description. He travelled into the different parts of Italy and the neighbouring countries, where the arts had begun to revive, to learn the processes which were there pursued; and he published, under the name of *Plictho*, a collection, which, according to Bischoff, is the first wherein the different processes were assembled, and which must be regarded as the primary impulse towards that perfection which the art of dyeing has since reached.\*

It is to be remarked, that in the work of Plictho there is no mention made of either cochineal or indigo; so that in 1548 these two colouring substances were probably not yet employed in Italy. Pliny indeed speaks of a substance which came from India, and to which the name of *Indicum* was given; but no use was made of it except for painting. It is, however, very probable that the Indians used it in dyeing; it appears, even, that the first which was employed in Europe was brought from the East Indies by the Dutch. The cultivation of it was first established in Mexico, and thence in the other parts of America,

\* "*Plictho dell' arte de tentori, che insegna tenger panni, tele banbasi e sede, si per l'arte maggiore, come per la comune. Venezia, 1548.*" This work has been translated into French under the title of "*Suite du tenturier parfait, ou l'art de teindre les laines, soies, fils, peaux, poils, plumes, &c. comme il se pratique à Venise, Gênes, Florence, et dans tout le Levant, et la manière de passer en chamois toute sorte de peaux; traduite de l'italien. Paris, 1716.*"

where it has acquired qualities superior to what comes to us from India.\*

For a long time Italy, and particularly Venice, possessed almost exclusively the art of dyeing, which contributed to the prosperity of their manufactures and their commerce; but by degrees this art was introduced into France. Giles Gobelin made an establishment in the place which bears his name. This enterprise was regarded as so rash, that the name of *Gobelin's Folly* was given to the establishment; and the success which it obtained so astonished our ancestors, that they believed Gobelin had entered into a compact with the devil.

The discovery of the scarlet dye may be regarded as the most remarkable era in the art of dyeing; not only by the lustre which distinguishes it, but also by the brilliancy which we can impart, by means of the same process, to several other colours. We have seen that the ancients gave the name of scarlet to the colour which they obtained from kermes, and which was very inferior in beauty to what we designate by the same appellation.

Some Spaniards having observed that the inhabitants of Mexico made use of cochineal for colouring their houses and dyeing their cottons, informed the ministry of the beauty of this colour; and Cortes received, in 1523, an order to promote the multiplication of the precious insect which produced it. The colour which cochineal gives naturally is, however, a rather dull crimson.

A little while after the cochineal became known in Europe, the scarlet process, by means of the solution of tin, was discovered. It is stated, that about 1630 Cornelius Drebbel observed, by an accidental mixture, the brilliancy which the solution of tin gave to the infusion of cochineal. He communicated his observation to his son-in-law, Kuffelar, who was a dyer at Leyden. He soon improved the process, kept it secret in his workshop, and brought into vogue the colour which bore his name.†

Soon thereafter, a German chemist, called *Kuster*, *Kuffler*, or *Kepfler*, found out also the scarlet process by means of the solution of tin. He carried his secret to London in 1643. A

\* The indigo imported into Great Britain from Calcutta now, is in general superior to the South American.—T.

† Grundriss der Farbekunst. Sigismund. Friedrich Hermsstadt.

Flemish painter named *Kloeck* or *Jean Glucq*, procured the knowledge of it, and entered into partnership with a family of the name of *Jullienne*, the last of whom died in 1767.\* This process was subsequently diffused over Europe. *Kloeck* travelled in the East, which, since the time of the Greeks, had preserved a remnant of manufactures; and he naturalized in Flanders the art of dyeing on wool and silk, which flourished there for a long time. M. Francheville fixes the death of this man, who was so useful to his country, towards the year 1550.†

The employment of indigo, which has been likewise a great acquisition to the art of dyeing, experienced more difficulty in its establishment than that of cochineal. It was severely prohibited in England under the reign of Elizabeth, as well as logwood, which was ordered to be burned whenever it was found in a manufactory. This prohibition was removed only in the reign of Charles II.

The use of indigo was equally proscribed in Saxony. It was treated in the ordinance issued against it (which reminds one of the decree against tartar emetic,) as a corrosive colour, and food for the devil. *Fressende Teufels*.‡

This is a grand example of the abuses into which an unenlightened administration, easily misled by the suggestions of personal interests, may fall. The blue dyers, who were in possession of the process with pastil and woad, represented that indigo would ruin the commerce of these two substances, which were native productions. This motive, which would be still specious in the eyes of several persons, readily determined the issuing a prohibition, which was soon to be eluded, at the expense of paying a tribute to the industry of other nations. The prejudice against indigo was also communicated to France; and in the Instructions of Colbert it is forbidden to put above a certain proportion of it into the woad vats.

Colbert gave to French manufactures, which had remained languishing under the stormy administrations of Richelieu and Mazarin, an impulse which soon advanced them beyond the progress of other nations. He called forth the most expert artists; he recompensed every talent; he established several

\* Notice sur la manufacture nationale de tapisserie des Gobelins; par Guillaumeau.

‡ Mem. de Berlin, 1767.

† Bischoff, Versuche, &c.

manufactories; and it may be remarked, that those of Vaurobais and Sedan were designated, in the letters-patent which were granted them, under the name of fine cloths of Dutch and English fabric. He published, in 1672, a code of instruction for dyers, which merits attention.\*

There are presented in this, first the motives which give importance to the object under consideration:—"If the manufactures of silk, wool, and thread, are those which serve principally to sustain and give value to commerce, dyeing, which communicates to them that beautiful variety of colours which makes them agreeable, imitating whatever is most lovely in nature, forms the soul, without which the body would have but a feeble existence.

"Wool and silk, which, in their natural colours, show rather the rudeness of the age, than the genius of man, and the refinement of our days, would command but a moderate trade, if dyeing did not impart to them that elegance which makes them be sought after and desired even by the most barbarous nations.

"All visible objects are distinguished or rendered desirable by their colours, which must be not only beautiful to give commercial currency to the stuffs, but also good, that their durability be equal to that of the fabrics to which they are applied."

In placing alongside of several salutary regulations, instructions for cultivators and artists, Colbert did homage to that feudal spirit, which multiplying with fiscal views the shackles of commerce, manufactures and agriculture, had impressed throughout nearly the whole of Europe the idea of regarding these bonds as indispensable. Instead of restricting himself to measures which should serve to guarantee the fidelity of the fabrics and the goodness of the colours,—instead of developing the germ of that honour which belongs to commerce, and which promotes its interest, he pushed the prohibitory regulation to the point of requiring, that the dyeing of black cloth should be begun by the dyers in the grand tint, and finished by the dyers of the little tint.—(*Teinturiers en grand teint, et en petit teint.*) The

\* "Instruction generale pour la teinture des laines et manufactures de laines, de toutes nuances, et pour la culture des drogues ou ingredients qu'on emploie." This work was reprinted in 1708, under the following title:—"Le teinturier parfait, ou instruction nouvelle et générale pour la teinture des laines et manufacture de laine de toutes couleurs, et pour la culture des drogues ou ingrédients qu'on y emploie."

former were allowed to have in their possession only a certain number of ingredients, while the latter were also restricted to a certain number. Neither the one nor the other were permitted to have Brazil wood, &c. It is true, indeed, that the sad effects of these prohibitions were tempered by the facility of evasion, as well as by the premiums awarded to those who made some advancement in their art, and whose discoveries being subsequently communicated to the public, produced modifications in the regulations. French manufactures lost their pre-eminence by the revocation of the edict of Nantes, which scattered them over the rest of Europe, leaving desolation in our factories.

Since this period, the department of administration charged with the superintendence of our arts and manufactures, has been constantly occupied with the means of repairing our losses, and of making our industry flourish. It has employed that plan in particular, which, with a judicious liberty, is the most efficacious of all, viz. the diffusion of instruction and scientific knowledge.

Dufay, Hellot, Macquer, were, in succession, charged with the duty of presiding over the art of dyeing; and to their labours we owe valuable improvements. Dufay was the first who formed sound, though incomplete ideas, on the nature of the colouring particles, and on the forces by which they adhered to cloth. He examined some processes with sagacity, and established the surest tests which could at that time be formed, for determining in a ready and practical manner the goodness of a colour. Hellot published a methodical description of the processes which are practised in the dyeing of wool, which forms still the best treatise we possess on this subject. Macquer gave an exact description of the processes executed in silk: he made known the combinations of the colouring principle of Prussian blue; he tried to apply its use to dyeing; and he furnished a process for imparting to silk brilliant colours by means of cochineal.

The solicitude of administration has had, in the judgment of foreigners, the success which it deserved. Anderson ascribes to the perfection of our dyes the superiority which some French manufactures have preserved over those of the nations which possess the finest wools;\* and Home thus explains himself:—

. \* History of Commerce.

“It is to the Academy of Sciences that the French owe the superiority which they enjoy in several arts, and especially in that of dyeing.”\* Several distinguished philosophers, indeed, have followed with equal success the example set by the Academy of Sciences.

Macquer had undertaken to publish a general treatise on dyes, of which he gave the prospectus in 1781; but the languor which for a long time announced his dissolution, prevented him from executing it. He who replaced Macquer in the administration of commerce, endeavoured, in the first edition of these *Elements*, to connect the theory of the phenomena presented by the art of dyeing, with the great discoveries which had effected at that period a revolution in chemistry; to make the application of it to the practice of this art; and to pave the way for a new career of advancement, by a more exact analysis of the properties of the substances which serve as agents in dyeing, or which have relations with the qualities of colours.

\* *Essay on the Bleaching of Cloth.*





# THE ART OF DYEING.

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## PART I. OF DYEING IN GENERAL.

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### SECTION I.

#### OF THE GENERAL PROPERTIES OF COLOURING SUBSTANCES.

#### CHAPTER I.

##### *Of the Theory of Colours, and of the distinctive Properties of Colouring Particles.*

THE physical theory of colours may appear foreign to a work, in which we are to consider only the properties which distinguish them, in reference to the agents which are employed in their application to the stuffs which receive them, and to the circumstances which produce in them changes or modifications. It may however be interesting and possibly useful to the discussions on which we are about to enter, to establish a connexion between the phenomena which the colouring substances produce, and those which the great Newton has analyzed in his "Optics."

We shall begin, then, by examining if the theory of Newton, concerning the colours assumed by transparent liquid or solid bodies, such as air, water, glass, according to the difference of tenuity of the plates which they form, and according to their respective density, can be applied to bodies constantly coloured, such as the colouring substances which are the objects of dyeing.

In order to represent the ideas of Newton, and the conse-

quences to be drawn from his observations, we shall enjoy the advantage of being guided by the treatise of Haüy, where physical knowledge is concentrated with equal elegance, clearness, and precision.\*

"In proportion as the transparent parts of bodies vary in size," says Newton, "they reflect the rays of one colour, and transmit the rays of another colour, for the same reason that thin plates and bubbles reflect the light, or transmit those rays; now, this is the principle of the uniform colours of all bodies."†

Newton, however, supported this induction merely by the experiments which he made on colourless substances. Delaval endeavoured to discover proofs of it in the operations which chemistry causes bodies to undergo, and in those of the art of dyeing.‡ Some doubts had been offered about this application of the theory of Newton, in the first edition of this work; since which time Bancroft has opposed to it a great number of facts.§ We shall avail ourselves of these several observations in the discussion which we are about to undertake, solely in the view of recalling to this interesting object the attention of those who can follow the traces of Newton. We must begin by forming an exact idea of the opinion which it is proposed to examine.

"In every body the particles are separated from each other by small interstices, which we call pores, and which contain different subtile fluids. These particles having a determinate thickness, repel the rays, which in penetrating them, are found in a fit (*retour*) of easy reflection, and the body thus assumes the colour, either simple or mixed, analogous to that of the reflected rays, and which depends on the degree of tenuity of the particles.

"In fact we have seen, that coloured rings are produced in the plates of solid bodies, as well as in those of liquids or fluids; and since every little space comprised in one of these plates reflects or refracts the light, it follows, that if this plate were

\* *Traité élémentaire de physique*, tome ii.

† *Optic*. lib. ii. part. 3. prop. 5.

‡ "Experimental Inquiries of the cause of the changes of colours in opaque and naturally coloured bodies." "Letter to the earl of Morton, on the relation between the specific gravity of several metals and their colours." This last work was honoured, in 1765, with a medal by the Royal Society.

§ *Experimental Researches concerning the philosophy of permanent colours*.

divided into a multitude of small fragments, each of these would still produce the same effect as when it was in continuity with the others. Now, as the particles of a body may be likened to the separated fragments of a plate, whatever may be said of this plate is exactly applicable to them also.

“ In speaking of the particles of bodies, it is not meant to designate their smallest molecules, or those which we call integrant molecules. In order to conceive what ought to be understood by the particles which reflect the light, we may suppose, with Newton, that the integrant molecules, already separated from one another by the pores, form, by means of the union of a certain number of them, other molecules of the second order, separated by more extensive pores; that these, in their turn, compose molecules of the third order, with interstices always more considerable; and thus in succession. Now the particles which reflect light in the ordinary state of a body, have a certain thickness, whence result separations to a certain extent between them: these particles are then considered as insulated, relatively to the adjoining ones. The *media* which intercept them, namely, the subtile fluids which occupy their pores, and the air which surrounds their outer surface, perform the function of two glasses, between which the plate of air in the experiment of Newton is comprised; for example, in a plate of mica of a perceptible thickness, there are particles of a certain order, which possess the property of reflecting the rays of a yellowish-white, and these exist naturally at sufficient relative distances for the light to act upon them, as if they existed alone. If we divide this leaf into leaflets of a certain degree of tenuity, we insulate the particles of another order, which will reflect other colours, as is confirmed by observation.

“ We have spoken, under the article *divisibility*, of a plate detached from a piece of mica, whose degree of thinness was such, that its primitive colour, which was yellowish-white, had passed to the most intense blue.”—*Häüy*.

Yet, whatever tenuity be given to carmine or indigo, by bruising, as Bancroft observes, the colour peculiar to each is not affected. We merely brighten it, by multiplying, according to Monge, the surfaces which reflect the white.

It may, indeed, be replied, that these substances are composed of homogeneous particles, which, notwithstanding the greatest

division at which we can arrive, producing the same effect as when they formed a continuity, whilst the mica has particles of a certain order, which possess the property of reflecting the rays of a yellowish-white; while on dividing a plate into thin *folia* to a certain degree of tenuity, we insulate the particles of another order, which reflect the blue.

We shall here venture to offer some observations.

1. This manner of supposing mechanical arrangements, in order to employ them in the explanations of physical properties, without directly proving them, may easily serve to prop hypotheses otherwise entirely destitute of probability.

2. This supposition of particles of different orders, which may reflect different colours in a homogeneous body, does not accord with the opinion of Newton, who ascribed all the colours obtained from plates of Muscovy talc, which is merely a mica, to the thickness which he mechanically gave to these plates; and who compares these colours to those produced by soap bubbles, according to the very variable thickness which they assume. By this opinion, indigo and carmine ought certainly to afford different colours, according to the tenuity of their parts; but we shall presently observe a circumstance, where it is difficult to suppose that the particles of indigo preserve, along with their colour, the same dimensions and the same density.

It is admitted, that a solvent must intervene in the dimensions of the molecules which reflect the colours; and this effect is employed to explain some changes of colours produced by acids and alkalies. "We may easily explain, on the principles laid down, the colours produced in certain liquors which are colourless, by the mixture of one of these liquors with the other, or the changes of colour which a liquor naturally coloured suffers in the same case. Thus, nitric acid dropped into alcohol, in which an infusion of roses has been made too feeble to communicate any hue, develops instantly a colour similar to that of the roses before infusion. The same acid, mingled with tincture of litmus, changes the blue into a lively red. Syrup of violets becomes green by the addition of an alkali. In all these mixtures, the union of the molecules of the two liquids forms mixed molecules, whose thickness is different from that of the component molecules, and occasions the reflection of the colour analogous to this thickness."

Newton specifies more particularly the cause of the changes of colour produced by acids and alkalies. "It is known," says he, "that saline menstrua are very proper for dissolving certain substances, and it is also known, that some of them precipitate what others dissolve; and as it is the nature of acids to attenuate and dissolve, and that of alkalies to thicken and precipitate, if the colour of the syrup of violets were of the second order, an acid liquid attenuating its particles would change this colour into a red of the second order."

Delaval has also tried to explain the action of acids and alkalies, by ascribing to the first the property of attenuating, and to the second that of inspissating. Let us examine, therefore, if the properties of acids and alkalies, and those of the solutions which they effect, authorize these explanations.

If, in the effect which they produce, the union of the two liquids forms mixed molecules, whose thickness is different from that of the component molecules, and determines the reflection of the colour analogous to this thickness, there must be a remarkable difference in this respect between barytes, which has a great specific gravity and a great fixity, and ammonia, which is, on the contrary, specifically very light and of an elastic disposition: there ought to be found a similarity of effect between some acids and some alkalies; yet barytes and ammonia produce the very same change. Sulphuric or phosphoric acid does not act differently from carbonic acid, on the substances whose colour they can alter.

The supposition advanced by Newton, that alkalies augment the thickness of the molecules, and that acids attenuate, will not appear well founded, to those who direct their attention to the properties of the solutions of colouring substances in acids or alkalies: the solution by alkalies properly presents, in the greater number of cases, more decided characters of attenuation than that which is due to acids, and it is for this reason that they destroy, in dissolving them, the greater part of the colours which have been fixed upon stuffs. It is only, therefore, for explaining certain changes of colour, that to alkalies is assigned a property which cannot be reconciled with observation.

We are now to examine a circumstance, where, notwithstanding a great difference introduced into the density, and a great attenuation of the colouring substance, this preserves unchange-

ably its colour. We shall confine ourselves to one example, although we could adduce many of the same kind. It is from indigo that we shall take it. If we dissolve indigo in sulphuric acid, we may dilute the solution by successive additions of water, so that it requires at least, according to the observation of Bergmann,\* “twenty pounds of water in a cylindric vessel of glass, seven inches diameter, to destroy the effect of the smallest drop of the solution.”

The molecules which always reflect the blue, ought however to pass through all the dimensions which exist between that of the solution of indigo, possessing much specific gravity, and that of water; they ought to suffer a greater and greater attenuation. Further, we may substitute the acetic acid for the sulphuric, by precipitating the latter with acetate of lead. A portion of the indigo falls with the sulphate of lead. This precipitate, which ought to have molecules much thicker, as well as the liquid which holds the indigo in solution merely by means of the acetic acid, possess equally the same blue colour.

Newton concluded from his observations, “that the corpuscles which produce black, must be smaller than any of those which produce other colours.”—His theory appears to us to lead even here to a result, which proves that a false application has been made of it. In fact, ink consists of molecules, which are a metallic compound in a state of precipitation, and which of consequence, according to the very idea of Newton, are placed in circumstances that announce the greatest compactness. If we dilute it with much water, the black passes to blue or violet. When the solution of indigo in sulphuric acid is much condensed, it appears absolutely black; by dilution with water it becomes blue; that is to say, by diminishing its condensation, or by doing the contrary of what the theory requires.

Hitherto we have discussed the opinion on the supposition that the colouring molecules act, by virtue of the form which belongs to them, in the liquids in which they are in solution, as we see is stated in the following passage of Haüy. “With regard to transparent and even coloured bodies, they seem to offer a middle term between limpid and opaque bodies. Their molecules reflect the rays of the colour under which they are

\* *Mém. des Sav. étr. tom. ix.*

presented to the eye, and at the same time these bodies transmit, throughout all their extent, other rays, which usually have the same colour as the reflected rays. Thus the molecules situated at the surface reflect one part of the rays which arrive at this surface, and transmit the rest; other molecules situated a little lower, reflect one part of the rays which have escaped the first reflection, then transmit the others; and thus in succession, to the last surface, where there still arrive a sufficiently great number of rays passing into the air, to give the body placed between the eye and the light a very sensible transparency. It thence results, that the greater thickness the medium has, the deeper is its colour, which agrees with observation.

"This supposition will not accord with the opinion which we must form of chemical combinations possessing liquidity, and in which all the properties become common among all the parts by their reciprocal action, whilst the equilibrium of the action is not disturbed. The figure which belongs to the different molecules allows no influence to be perceived till they approach the term where they must pass to the solid state: It is then, for example, that water, which tends to congeal, acquires an expansion due to the effort which it makes, in order that its molecules, in losing their liquidity, may assume an arrangement determined by their surfaces.

"Experiments made by Delaval appear to prove, that the effects attributed to the distinct parts of the colouring substances in solution, do not depend on their individual reflection. He filled a flask, of a square form, with a coloured liquid, after having covered three of its sides and the bottom with a black paint; and he observed, on looking to the liquid by the free face, which formed a right angle with his window, to prevent the reflection from the posterior surface, that the above liquid appeared black, whatever might be its proper colour. Glasses having the same form, and differently coloured, equally appeared black when they were covered with a black cloth, with the exception of one face which was left free, to admit the incident light. If their mass be considerable, they thus also appeared black; but their fragments applied to a white ground, exhibited the colour peculiar to them."\*

\* Mem. of the Liter. and Philos. Soc. of Manchester, vol. ii.

He thence concludes, that coloured liquids and glasses are seen in their proper colours only by rays reflected from their posterior surfaces; so that it is the rays which have traversed the coloured liquid or glass, which give the sensation of colour by transmission or reflection.

He makes a remark, whose application is found in this place. "If a small quantity of colouring substance is mixed with a medium which has no colour, the mass appears dyed with the colouring substance. But if we add a great quantity of this colouring matter, the mass appears black; consequently, in ascribing to the colouring substance the power of reflection, we advance a contradictory and inexplicable proposition; for we affirm, that the more of the substance, having the power of reflection, the incident light encounters, the less light is reflected; so that if the colouring substance be very abundant, there is no longer any colour but a black."

In order to extend this theory to opaque coloured bodies, Delaval supposes that they are always composed of two substances, one of which is white, and the other, which is coloured, possesses transparency, so that the rays of a certain colour which traverse it, are reflected by the white surfaces that they meet. When white molecules do not separate those which are coloured, it is enough if there be present any medium whatever possessed of a different density; as Newton has shown that two transparent substances, of a widely different density, produce an opaque body. Delaval thus explains the colour of gold and metallic oxides.

This explanation is very specious, and satisfies the greater number of observations. Nevertheless its application appears to us too general, because it requires us to suppose, between the coloured molecules of the metals, the existence of a *medium*, which the other properties do not indicate, and because other causes may produce the effect here ascribed to it.

In recapitulating what has been said, we find, that in order to explain the different phenomena presented by coloured bodies, 1st, we consider, in a general manner, *the colouring molecules of a body as insulated, relatively to those which adjoin them, and the media which are interposed; viz. the subtile fluids which occupy their pores, and the air surrounding their exterior surface,*



*as two glasses, between which is comprised the plate of air, as in the experiment of Newton.*

2. It is admitted, however, that in the solutions which experience changes of colour by the action of acids and alkalies, the union of the molecules of the two liquids forms mixed molecules, whose thickness is different from that of the component molecules, without explaining the uniformity of effect of those acids and alkalies which differ most in their specific gravity, fixity, and volatility.

3. It is presumed, on the contrary, that in the solutions, combinations, and precipitations, where the substances preserve the same colour, there occurs no alteration in their dimensions, applying to the colouring parts the theory of No. 1., although the state in which they exist be equally the effect of a reciprocal action, and although there be equally a combination.

4. In all the cases of transparency, the colouring molecules are supposed to act individually on the rays of light; and experiment seems to prove, that the reflection of bodies which are not opaque, takes place only at their anterior and posterior faces.

The effects observed in the solution of water in air, and in its precipitation, appear to us capable of illustrating the properties of solutions relatively to light.

When damp air has been compressed in a globe, according to the experiment of Kratzeinstein related by Saussure,\* and when we restore the freedom of communication, this air, which, placed between the eye and the light, exhibited at first only a pure transparency, causes vapours to be perceived, which have the colours of the rainbow at the moment when the compression is removed; and it resumes its transparency by a new compression.

This phenomenon is not difficult to analyse. When the air, saturated with humidity in a state of compression, is suddenly liberated, it produces by its dilatation a degree of cold, which causes the precipitation of a part of the water which it held in solution. Compression produces a contrary effect, by the heat which accompanies it.† Saussure remarks that the phenomenon due to the vapours lasts only an instant, because the temperature becoming fixed, the state of solution becomes equally so.

Light, then, experiences no peculiar reflection or refraction

\* Essai sur l'hygrom. sect. 209.

† Stat. chim. tom. i. p. 163.

from the water or air while the solution exists; and it is only when these two elements acquire a peculiar existence that this effect begins. Is it not natural to ascribe to other solutions what is here observed in that of water? On the other hand, can we compare the constant properties of coloured substances with the variable and transient effects owing to the refraction and reflection of the molecules in simple juxta-position?

Delaval made a great many experiments to prove, "that the more considerable the density of constantly coloured bodies is, the greater also is their power of reflection (every thing else being equal) for reflecting the least refrangible rays; that, on the contrary, when they have less density, they can proportionally reflect only the less refrangible rays; and consequently they must exhibit different colours, according to the order of their density."

He makes choice particularly of metallic bodies to prove, "that they differ as to colour, exactly in the same gradation as in density; the densest body being red, that which is immediately of a less density being orange-yellow," &c.

A little attention, however, is sufficient to convince us, that there is no relation between the specific gravity of metals, or of glasses coloured by their oxydes; and their colours. Delaval regarded, with Newton, the solution of metals as a simple division of their molecules, without regard to their oxydation, the theory of which was then unknown, and on which principally depend the changes of colours in their solutions and oxydes. To establish his opinion, and to make the peculiar colour of every metal coincide with its specific gravity, he selected that state of solution and oxydation which best suited his views. We refer to the treatise of Bancroft for a detail of the facts hostile to the opinion of Delaval.

Newton ascribed the colour of white metals "to their excessive density, by virtue of which they seem to reflect almost all the incident light, unless, when dissolved in suitable menstrua, they be thereby reduced into very small particles, when they become transparent."\*

If, from the density, we judge of the effect which silver ought

\* The brilliant white of potassium and sodium, bodies of little density, seems adverse to this idea of Newton.—T.

to produce on light, its solution in nitric acid, which can take up a great quantity of it, and can be diluted with water as much as we please without decomposition, ought, in passing through different densities, to acquire the property of reflecting different colours. It remains, however, colourless and transparent, although, according to the observation of Wollaston, the refracting quality of the metallic solutions varies with their different degrees of concentration.\* It ought to tally with the density and attenuation of the solutions or precipitates of cobalt, nickel, and manganese, which, like silver, void of colour in the metallic state, acquire it very intensely and very variously in their oxydation and precipitation.

The considerations now presented lead us to believe that we ought not to confound the fugitive colours produced by the reflection of plates, which follow the laws described by Newton, with the colours which continue, notwithstanding the changes of density and thickness. These appear to depend on properties, in which the peculiar affinity for the different rays of light has an influence which resists that of the dimensions and the density. On examining the facts, we perceive that condensed oxygen exercises a great power in this species of affinity. A variable proportion of it, affecting in an insensible manner the specific gravity of the metallic oxydes, produces in them great changes of colour. In like manner, a little oxygen, conveyed by muriatic acid to colouring substances, either makes their colours disappear, or produces in them considerable alterations; whilst other combinations, for example that of alumina, which precipitates the greater number of colouring substances in the form of lakes, and which, according to the ideas of Newton and Delaval, ought to give considerable density to these substances, preserves meanwhile their proper colour, merely concentrating it by the condensation which the earth occasions.

The very experiments of Newton prove, that the peculiar affinity of different substances has a great influence on their relations to the rays of light; since, according to him, their refractive power is proportional, not merely to their density, but also to their inflammable disposition. This proposition ought not to be taken with too great latitude; for phosphorus,

\* Phil. Trans, 1802. Ann. de chim. tom. xlv.

which is very inflammable, has no great refrangency. It follows, however, from the very observations on which the doctrine rests, that there is a great difference of action, according to the affinity of the bodies for the rays of light.

The interesting experiments of Dr. Blair likewise prove the peculiar power of the affinity:—When light passes from any medium whatever into a vacuum, the red rays are the least refrangible, and the violet are at the other extreme; but if light passes from one medium into another, he shows, that it is the quality or particular nature of these media that determines which of these rays shall be the most refrangible, or if they shall be equally so. The green rays occupy the middle of the spectrum in the dispersion occasioned by crown glass; they are found among the least refrangible by the dispersive action of flint glass; but in muriatic acid these rays are found, on the contrary, on the side of the violet or the most refrangible. It thence happens, that the order of the colours is reversed in the secondary spectrum, formed by a combination of crown glass with the liquid.\*

If we depart, in these considerations, from the consequences to which physical observations have led—if we believe that we must resist, in this particular, the authority of the great Newton, and that of his illustrious interpreter, it is with regret; for we feel how important it is to connect all the effects due to the reciprocal action of bodies, and we hope that future experiments will fill up the space which here seems still to separate natural philosophy and chemistry. Meanwhile, we shall confine ourselves to the results of this last part of the science, which treats of the properties of bodies.

In the metallic oxydes, and in several mineral substances, all the parts are equally coloured; but this is not the case with vegetable or animal substances. The colour in the latter is usually owing merely to particles, which are mixed or combined with those constituting the bodies themselves; and vegetables contain sometimes different colouring molecules at different periods of their growth, or in their different parts.

The colouring molecules of vegetable and animal substances are almost the only ones employed for the purpose of dyeing;

\* *Bibliot. brit. tom. 8.*

but they are often modified by the use of intermedia. Such are the substances designated in this treatise by the name of colouring particles.

These colouring particles do not exhibit, in their composition, the simplicity of mineral substances, nor does oxygen affect their colours in the same way. We shall examine, in one of the following chapters, in what manner this principle acts upon them so as to alter their nature.

Some chemists have regarded iron as the cause of all vegetable and animal colours; and Adolphus Becker employed, in support of this opinion, considerations derived from the property which this generally diffused metal possesses, of assuming a great number of colours in the states of oxyde, solution, and vitrification.\*

Iron, in fact, appears to be contained in all vegetable and animal substances, but in extremely small quantity. Oak, one of the vegetable substances which ought to yield the largest residuum, leaves in its combustion only 1-200th of its weight of ashes; and these ashes do not contain 1-200th of iron. Can the rich and splendid colours with which vegetables are enamelled be explained by so minute a proportion? Is there in reality any relation between the changeableness of some of these colours, by acids, alkalies, and air, and the uniform succession of colours which iron assumes according to its degree of oxydation?

The opinion which we are combating might indeed be supported by the suffrage of Bergmann, who supposed he had proved that indigo owes its colour to the iron which it contains;† but we may be permitted to reply, that it is easy to show how this great chemist had deceived himself on this subject. By means of the alkaline prussiate, he obtained, from the ashes of an ounce of indigo, from 30 to 32 grains of prussian blue; and he estimates the iron which this contains at 18 or 20 grains. But in other places he proves, that the iron contained in a substance forms at most but a fifth part of the prussian blue which we procure from its solution, and everywhere else he employs this valuation. We must therefore reduce to six grains

\* Specimen sistens experimenta circa mutationem colorum quorundam vegetabilium a corporibus salibus, cum corollariis; auctore J. F. Adolpho Becker, 1779.

† Analyse chimique de l'indigo. *Mém. des Savans étr. tom. ix.*

the iron he obtained from an ounce of indigo. In the experiments which follow the above, he proves, that the greater part of this iron may be dissolved by muriatic acid, without the colouring particles being affected; so that the larger share of this metal does not enter into their composition. From this it clearly follows, that the colouring particles of this substance must contain a quantity of iron so small, that can have but little influence on its colour.

The means of chemical analysis which we possess are so far from enabling us to determine the composition of the colouring particles with sufficient precision for showing to what principles they owe their properties, that we often observe a very different composition giving rise to a colour of the same kind. The particles of indigo differ much from those which colour several flowers blue. A great number of yellow substances afford colours almost similar in appearance, which notwithstanding differ much in their properties.

There are simple colours, and there are others arising from the mixture of these colours, which are consequently compound. Newton has given a general rule for forming any colour whatever, by means of other prismatic colours. Le Blond has proved that we may procure all the colours which the art of the painter can desire by the mixture of red, blue, and yellow.\* Dufay has shown that the same effect may be obtained in dyeing; and he has thence concluded, that there was in nature only three primitive colours, which gave origin to all the rest. This opinion has been embraced by several philosophers; but it does not appear to be sufficiently established.

Between simple colours and colours formed by the union, of different rays, there is this difference:—the former, viewed through the prism, retain their simplicity, while the latter are decomposed. The green produced by the rays of this colour suffers no decomposition by the prism. It has, therefore, the character of a simple and primitive colour. But the compound green is separated into yellow and blue.

Although the green formed in dyeing results from a mixture of blue and yellow, we must not consider all the greens as combinations of the two species of colouring particles. Thus, the

\* *L'Harmonie du coloris dans la peinture, réduite en pratique.*

green oxyde (hydrated oxyde) of copper cannot be owing to molecules of a different nature; and the green of plants is undoubtedly produced by a homogeneous substance, in the same way as the greater number of hues which exist in nature. This colour owes then its origin sometimes to simple rays, and sometimes to an union of different rays; and some other colours are in the same predicament. Were the green of plants due to two substances, one of which is yellow and the other blue, it would be extraordinary if we could not separate them, or at least change their proportions by some solvent. There are, however, some substances which contain colouring parts of different species; madder, for example, as we shall see in the second part. (NOTE A.)

The green, which we assume as an example of a truly compound dyeing colour, shows that the colouring molecules cover only one part of the surface of the stuff, although this may appear of a full and uniform colour; for, after the stuff has been dyed blue, the yellow parts fix themselves on it, and produce the green; and although the dyeing has been begun with yellow, if a yellow of little permanence be employed, it may be destroyed by air, and especially by chemical agents, while the blue remains unaffected: which proves that it is on the stuff, and not on the indigo, that the yellow particles have been principally fixed.

Hence we see, that in order to procure the sensation of a simple colour, the rays of the different colours require merely to be approximated. In fact, we may produce a uniform colour by the exact mixture of wools of different hues; and in painting we obtain simple colours by the mixture of different ingredients, which do not chemically combine.

The colouring particles form different combinations, and they are applied either alone, or previously combined with other substances, to wool, silk, linen, or cotton. The art of dyeing consists in employing the affinities of the colouring particles so as to extract, dissolve, and thereafter apply and fix them to the substances to be dyed, which will be distinguished in this treatise by the name of *stuffs*, whatsoever may be their nature and their form.

It has been proposed to arrange colouring particles into extractive and resinous; but this division conveys only incomplete

and false ideas of their properties; for there are colouring particles which, being insoluble in water, might be regarded as resinous, and yet they do not dissolve in alcohol. Such are, the red portion of carthamus, (safflower,) which dissolves merely by means of an alkali; and indigo, which, insoluble both in water and alcohol, becomes soluble in alkalies only under certain circumstances; but it dissolves readily in sulphuric acid.

The colouring particles which are soluble in water cannot be compared to the mucilaginous and extractive parts of vegetables, since the property of dissolving in water, like these substances, gives no idea of the properties which it is essential to discover in them; such as their relations to the chemical agents employed in dyeing, to air, to light, and to animal and vegetable substances.

It is, moreover, an abuse injurious to the progress of sound theorizing, to seek an explanation of the properties of colouring substances in the mucilaginous, resinous, earthy, saline, and oily parts which may be supposed to enter into their composition, as Poerner particularly has done.

We have just seen, that in trying to account for the causes of colours, and the nature of the colouring particles, two inconveniences have arisen: the one, from the attempt to explain the action which the molecules of colouring substances exercise on the rays of light by their density and thickness, without having any means of determining these circumstances, and without taking into view the affinity arising from their chemical composition; the other, to compare, from some slight relations, the colouring particles with the mucilages and the resins, and to seek to explain their properties by the parts supposed to enter into their composition; whereas their colouring properties ought to be determined by direct experiments, and not be explained by an imaginary composition. We depart from true theory, which is solely the result of observation, when we ascribe to laws purely mechanical the adherence of the colouring particles to the substances which they dye, as well as the action of mordants, and the difference between permanent and fugitive colours. Hellot, to whom otherwise we are indebted for the best practical treatise extant on dyeing wool, has fallen into a complete illusion on this subject, and his theoretical ideas have often influenced his observations, and the principles which he



has laid down, as we may ascertain by the perusal of his work. We may judge of his theory by the following passage:—"I believe it may be laid down as a general principle of the art now treated of, that the whole invisible mechanism of dyeing consists in dilating the pores of the bodies to be dyed, in depositing within them particles of a foreign matter, and in keeping them there by a species of coat, (*enduit*,) which neither water, rain, nor the rays of the sun, can affect; in selecting colouring molecules of such a tenuity that they may be retained sufficiently incased in the pores of the subject, laid open by the heat of boiling water, then contracted by cold, and farther coated with a species of cement, (*mastic*,) which is left in the very pores by the salts chosen to prepare them. Hence it follows, that the pores of the fibres of wool, from which we have fabricated or are going to fabricate stuffs, ought to be cleansed, enlarged, coated over, then contracted, in order that the colouring atom may be preserved in them nearly as a diamond in the collet of a ring."\*

We have reason to be surprised that Macquer should have adopted the ideas of Hellot. "Here would be the place," says he, "to explain the manner in which mordants act in dyeing, and to develop the cause of fast and fugitive dyes: but these objects have been treated with so much sagacity by M. Hellot, that I think it my duty to refer my reader to him."†

Dufay, however, had already perceived, that the colouring particles were naturally disposed to contract a stronger or weaker adhesion with the fibres which received them;‡ and he remarks very properly, that without this disposition the stuffs would not take a colour similar to that of the dye-vat, or divide equally with it the colouring particles; whereas the liquor of the bath becomes sometimes as limpid as water, giving up all its colouring matter to the stuff; "which seems," says he, "to indicate that the ingredients have less attraction for the water than for the particles of the wool." He adds, that several other phenomena may be accounted for in the same way; but that such an explanation leaves still much to be de-

\* L'Art de la teinture des laines, p. 42.

† L'Art de la teinture en soie, avant-propos, p. 8.

‡ Observations physique sur le mélange de quelques couleurs dans la teinture.—Mem. de l'academ. 1737.

sired, and that he would abandon it without difficulty were a more probable one proposed.

Bergmann is the first who referred the phenomena of dyeing entirely to chemical principles.\* Having dyed wool and silk in a solution of indigo, in sulphuric acid much diluted with water, he explains the effects which he observed in this operation, by ascribing them to the precipitation occasioned by the greater affinity of the wool and the silk for the blue molecules, than of these molecules and the acidulous water. He remarks, that this affinity of the wool is powerful enough to deprive the liquid entirely of its colouring particles; but that the feebler affinity of the silk can only diminish the proportion of these particles in the bath; and he shows, that on these different affinities depend both the permanence and intensity of the colour.

This is, in fact, the legitimate manner of viewing the phenomena of dyeing, which are true chemical phenomena.

A short while thereafter Macquer adopted this theory, and made just applications of it to the action of mordants, and particularly of alumina.†

Whatever may be the physical cause of colours, the colouring particles, which it is the object of the art of dyeing to apply to stuffs, possess chemical properties distinguishing them from other substances dependent on the affinities which their particles collectively exercise, as well as on the reciprocal action of these particles, and on their constitution, which disposes them more or less to assume the solid or the liquid state.

By virtue of these properties, they dissolve in different liquids, they combine with acids, alkalies, oxydes, with some earths, and especially alumina; they frequently precipitate the oxydes and alumina from the acids which held them in solution; in other circumstances they even form super-compounds with the salts; sometimes they unite immediately to the stuffs; more frequently they form with these substances a combination much more intimate through an *intermedium*, or even they do not combine with it except through the *intermedium*; the intermedium modi-

\* Analyse de l'indigo. Mem. des Savans etrang. tom. ix.; Mem. envoyé pour le prix proposé en 1776, et dans les notes sur le traité de Scheffer.

† Diction. de chim. 2nd édition, au mot teinture, 1778.

fyng more or less their colour, their other properties, and even their composition.

The difference in the affinity of the colouring particles for wool, silk, and cotton, is sometimes so great, that they refuse to combine with one of these substances, whilst they combine very well with another; thus, cotton takes no colour in the bath that dyes wool scarlet. Dufay got a piece of stuff made, the warp of which was wool, and the weft cotton; he passed this stuff through the fulling-mill, to ensure the same preparation to the wool and cotton; but the wool took the scarlet dye, and the cotton remained white. It is this difference of affinity which makes it necessary to vary the preparations and the processes, according to the nature of the substance which we wish to dye of a particular colour.

If the effects of the *intermedia* employed in dyeing, and if the fixation of the colouring particles on a stuff by itself, or by means of an intermedium, be owing to the combinations which are formed, we must still refer to chemical combination the changes produced, by acids and alkalies, in several vegetable colours, which chemists employ for verifying the nature of different substances. We may compare the resulting compounds to neutral salts, which possess qualities distinct from those of their components, but in which one of the components may be in excess, so as to cause its properties to predominate. This state of combination is observed between the colouring particles of cochineal and the acidulous tartrate of potash, or cream of tartar. On evaporating slowly a solution of this salt in a decoction of cochineal, crystals are formed, which retain a fine ruby colour, much more intense and more lively than that of the liquid in which they were formed.

The reciprocal action of acids and alkalies being much greater than that which they exercise in particular on the colouring particles, they can mutually saturate each other, and then the resulting compound has little effect on the colouring particles, so that the changes which had been produced by one of the substances disappear when it is neutralized by an antagonist substance.

Blue colours are not the only ones which can pass to red by the agency of acids, and to green by that of alkalies; the most part of the red colours, that of the rose, for example, are exalted by acids, and pass to green by alkalies; and some green colours,

such as that of the decoction of burdock, according to the testimony of Nose,\* and the green juice of the buckthorne berries, (*rhamus catharticus*) according to Becker, reddened also with acids.

This property, common to the most ordinary colours of vegetables, appears to prove that there is a close analogy between the greater part of their colouring matters; nor is it without foundation that Linnæus† thought the red colour owing to an acid, of which he maintained the existence; but there are also several vegetables which contain a free acid, without possessing a red colour.‡

In the combination which the colouring molecules form with the stuff, they preserve only a part of their original properties; on being associated with alumina, with the oxydes, and some other substances, they are somewhat modified; but the properties of the latter combinations are further modified when they unite with the stuff.

These modifications are analogous to what is observed in other chemical combinations; but they are subject to a peculiar degradation from the action of air and light; sometimes, on the contrary, they receive from these agents a new lustre, or a different shade: there are also agents which, after combining with the colouring particles, alter the colour which they first produced, making it pass to yellow, and then destroy it; such in particular is oxygenated muriatic acid (chlorine;) it acts by means of the oxygen which it yields, and consequently differs in nothing except intensity from that of the atmospheric air.§

It follows, from what has been stated, 1. That the colouring molecules have affinities which produce their solution and their

\* Versuch einiger Beyträge zur Chemie.

† Amœnitatum acad. tom. iv.

‡ There are flowers whose colour appears to be naturally modified by a very feeble acid, without being decidedly red: such is the flower of violet, whose violet juice becomes blue when we leave it for some time in a tin vessel, probably because the acid which it contained combines with a portion of oxyde on the surface of the tin; such also is the flower of the mallow, which becomes blue by simple drying. The primitive colour is restored by the addition of a very small quantity of acid."—*Observ. physico-chim. sur les couleurs, par Opoiz. Journal de physique, tom. viii.*

§ This theory is no longer tenable, since it is known that dry chlorine, even though condensed into the liquid state, does not bleach dry litmus paper. When moisture intervenes muriatic acid is formed, and oxygen evolved; to the action of which body on the colour the bleaching effect is to be ascribed. Water is the source of the discoloration both in the ancient and the modern process of bleaching.—T.

combination, the effects of which, combining with those of their own constitution, form the differences that distinguish them from each other.

2. That they unite directly with the stuff, or by the aid of an intermedium; but the stuff has relations with them according to its nature.

3. That, in combining with a substance, they experience a change which modifies their colour, besides the modification resulting from the shade peculiar to the substance to which they combine.

4. That the colouring molecules differ not only from one another by these different dispositions, but likewise by the ulterior changes which they may suffer from the action of other substances, and particularly from that of the air and light.

In order to establish, on these grounds, the principles of the art of dyeing, so as to explain the peculiar phenomena which it presents, to guide ourselves in its practice, and to obtain the surest, easiest, and most economical processes, either for executing known operations, or for fulfilling the demands of the consumers, and improving the art, we shall in this section examine more particularly the effects arising from the action of substances which serve as *intermedia*, and those produced by the agents which may affect the nature of the colours.

But stuffs possess different relations with the colouring particles, and they must receive preparations preliminary to the operations of dyeing: under this point of view, we shall examine them in the second section.

The third section will be devoted to the art of bleaching linen and cotton by the oxygenated muriatic acid, (chlorine.)

We shall be occupied, in the fourth, with the manipulations of dyeing in general, and the means by which we can ascertain the goodness of colours.

We shall present, in the fifth, a summary account of the principal ingredients employed in dyeing, in reference to dissolving, modifying, and fixing the colouring particles.

After having thus exhibited, in the first part of this work, the general facts which are to be applied to particular operations, we shall detail, in the second part, the processes of dyeing, arranging them into *genera* and *species* of colour. Here we shall examine every colouring substance; we shall apply to the different

dyes the principles established in the first part ; we shall unfold the processes of the art, and independently of the explanations, we shall endeavour to improve it by direct experiments. We shall then try to harmonize the results of experiment with the principles of chemistry ; but we shall stop whenever these principles cannot conduct us to satisfactory explanations, or we shall confine ourselves to conjectures, to be verified by the future advancement of the science.

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## CHAPTER II.

### *Of Mordants.*

THE term *mordant* is given to those substances which serve as *intermedia* between the colouring parts and the stuffs which they dye, either for facilitating or modifying their combination. This word is rendered appropriate by the use which even the ancients made of it.\* We may distinguish, under the title of *alteratives*, the ingredients which are employed merely with the view of changing the shade.

Mordants merit the greatest attention. It is by them chiefly that we diversify the colours, give them more brilliancy, fix them on the stuffs, and render them more durable.

A mordant is not always a simple agent, but in the mixture composing it different combinations are sometimes formed, so that the substances which have been employed do not act immediately, but by the resulting combinations.

Sometimes the mordant is mingled with the colouring particles ; sometimes the stuff is impregnated with it before being exposed to the dyeing bath. On other occasions these two methods are combined. We may dye in succession with liquors which contain different substances, the last of which acts only on the parts with which the stuff has been imbued by the preceding operation. One solution, which is to yield its basis to the stuff has need of heat ; another requires the operation to be made in the cold. The mordant is frequently an oxyde ; in which case its properties may vary, not only accord-

\* Ameilhon. mém. de l'institut. litter. tom. iii.

ing to its actual condition, but also according to the action of the substances with which it is associated, and even according to the circumstances of the operation. It is by the determination of all these conditions that chemistry can particularly direct the art of dyeing, can establish its processes in a constant manner, removing from it whatever is useless or prejudicial, and transferring to one kind of dyeing what is found efficacious in another.

We shall describe, in the fifth section, the essential properties of the chemical agents of which the greatest use is made in the quality of mordants: we shall determine, in the second part, the particular effects which they produce on every species of colouring substance, detailing every fact which experience has taught concerning those operations of dyeing in which they are employed. At present we shall confine ourselves to the development of the general observations which have been made on their action.

There are colouring substances on which acids and alkalies appear to have but a feeble action, which are soluble in water, and combine immediately with stuffs; such are several dun colours, extracted from woods and roots, and the husks of the walnut. These substances serve, therefore, the purpose of dyeing without the aid of any mordants. There are some, again, which dissolve only by alkalies, as, in particular, the safflower.—Its colouring part quits the alkalies, and fixes on the stuffs, when those are saturated with an acid. The anotto, which dissolves easily by means of an alkali, abandons it to combine with the stuff, without the necessity of employing an acid. When indigo is deprived of oxygen, it becomes yellow, and is then soluble in alkalies. Stuffs may abstract it also from the alkalies, and then it resumes its blue colour, through the agency of oxygen. Dyes made with these colouring substances have no need of auxiliaries. But the greater number combine only in small quantity with the stuffs, when a base does not serve as an *intermedium* to their union. They adhere feebly to it, and resist much less the causes of destruction.

The substances employed as mordants should therefore furnish a base which attaches itself to the stuffs and to the colouring particles, and which resists their redissolution and destruction. As to those substances, however, which occasion merely some modifications in the colours, it is sufficient for them to be re-

tained in small quantity in the combination formed between the stuffs, the mordant, and the colouring matter. Hence, although alteratives act equally by combining, they should be distinguished, however, from mordants, which serve to fix the combination.

Acids can in general dissolve the colouring substances, but as they do not themselves possess the property of combining with the stuff, they cannot serve as bonds of union; on the contrary, they usually carry off the colouring particles which had been retained by the stuff, and they contribute to the colour which is fixed, only in the quality of alteratives, by uniting in small quantity to the coloured combination.

The alkalies, among which we must comprise the earths that produce saturation with acids, can combine with the most part of colouring substances; but, in order to ascertain the effects which they ought to produce according to their differences, and to compare them with those due to the acids, we must direct our attention to the properties of the combinations which depend on those of their elements.

While reciprocal affinity produces an union, the dispositions of the substances to solidity or liquidity are preserved in the combinations, with the differences proceeding from the condensation which they experience.\*

It thence results that the alkalies, which possess much solubility, ought to form soluble combinations with the colouring substances which have an affinity for them; but those which have little solubility ought, on the contrary, to produce insoluble combinations.

These considerations, which are supported by the results of the reciprocal action of acids and alkalies, and by the properties of the combinations in general, lead us to distinguish the effects of the different bases. Potash, soda, and ammonia, cannot serve as *intermedia* to fix the colouring substances on stuffs; but they may, as well as acids, effect the solution of colouring substances on which they have an action. Their affinity with the stuffs should also tend to operate their solution. It is only as alteratives that these alkalies can enter into coloured combinations. If they produce some precipitation in the watery solutions of colouring substances, it must be merely by separating a body much more soluble, from another in itself slightly soluble,

\* Essai de statique chimique.



or by occasioning some change in a substance of somewhat unstable composition.

The other alkalies, namely, lime, barytes, strontian, and magnesia, which possess little solubility, or a much greater tendency to solidity, appear fitter to serve as mordants. In fact, these alkaline earths have sufficient affinity to form, with colouring substances, combinations which are precipitated from their solution; but they considerably affect their colours by their alkaline properties. They possess too weak an affinity to enter into an insoluble combination with the stuffs; so that, far from promoting the union of the colouring particles, on the contrary they obstruct it, forming insulated precipitations.

Magnesia, which is insoluble, afforded the prospect of being usefully employed as a mordant. In order to try it, acetate of magnesia was mixed with an infusion of brazil wood. A precipitate took place of a dull violet colour. After ascertaining the faculty it possesses of falling down with colouring substances, cotton was impregnated with the above salt, as is done with the acetate of alumina; but this cotton took no more colour than if it had received no mordant. Wool treated with acetate of magnesia, did not derive from it the property of fixing the colour of madder; no more did silk. It appears, then, that the alkalies in general can serve only as solvents or alteratives; but in this latter quality, those which have the least solubility should be the most efficacious. The same thing is true of the acids; whence the utility of the bitartrate of potash in several processes.

The body which possesses in an eminent degree the properties suitable for a mordant is alumina. Insoluble when it does not experience the action of acids or alkalies, it has a strong disposition to combine with the colouring particles; it does not act on their colours as the alkalies do, but it preserves very nearly their natural hue. It separates also much more easily from the acids which hold it in solution, than the alkaline bases do.

To be convinced of the property which alumina possesses, of combining with the colouring particles, we have only to agitate alumina, precipitated from the sulphate of alumina by an alkali, with an infusion of brazil wood, when all the colouring particles separate from the water, and remain fixed in the earth. It is

this combination which forms some lakes, and particularly the *stils de grains*.\*

This is not the method, however, in which it is directly employed for the composition of the most part of lakes.

A decoction of the colouring substance from which we wish to obtain a lake, is mixed with a solution of the sulphate of alumina. There is usually formed a precipitate, which carries down a portion of the colouring substance. With some colouring matters, however, no precipitate ensues. To cause, or to complete it, the acid of the salt is saturated with an alkali, when the alumina falls down, retaining in combination with it the colouring substance; it is this precipitate, whose colour varies with the substance employed, which forms the lakes, after sufficient washing to carry off the saline particles. For the *stils de grains*, the decoction, mingled with the sulphate of alumina, is passed through a calcareous carbonate, which serves, at least in part, to decompose the sulphate of alumina; or through a clay, whose action on the sulphuric acid contributes also to the decomposition of the alum, and to the precipitation of the lake. What occurs here by the action of the alkali or the clay, which tend to seize the acid, is effected in dyeing by an opposite action, by the affinity between the stuff and the coloured alumina.

The affinity of alumina for the different stuffs may be easily proved. If an animal substance be dissolved by an alkali, and if with this solution alum be mixed, the animal substance precipitates in combination with the alumina. The same combination is formed when, after mixing gelatin with a solution of sulphate of alumina, an alkali is poured into it.

The combination of alumina and the animal substance may be combined with a colouring substance. For example, when, in the preceding experiment, the decoction of a colouring substance, such as brazil wood, is mixed with the solution of sulphate of alumina and gelatin, the coloured precipitate thus obtained represents the combination which is formed with the stuffs in those dyes where a mordant is employed.

Although it cannot be proved in the same manner, that alumina enters into combination with linen and cotton, yet the effects

\* *Traité théorique et pratique sur l'art de faire et d'appliquer les vernis, &c., par Tingry, tom. ii.*

which aluminous mordants produce upon these substances, leave no doubt that a combination with alumina is formed. Hence, by means of alumina, colouring substances which could not be fixed, or would be speedily destroyed, quit their solvent, form with the alumina more saturated and durable colours, and even when the colour has disappeared, the stuff still retains the alumina, which can fix new colouring substances, and impart to it the requisite properties. Bancroft relates, that having impregnated with acetate of alumina one part of a cotton web, while the rest of it had no mordant, and having dyed this cloth with saffron, he exposed it on the grass: The colour soon disappeared on the part which had received no mordant, and some time afterwards on the portion which had been imbued with the mordant. He then dyed the cloth anew with saffron, when the exposure on the grass produced the same effect. Finally, after a third dyeing, the mordant still gave the same faculty to the portion of the cloth to which it had been applied. Hence alumina remained fixed, notwithstanding the three dyeing operations.

It is manifest, therefore, when a stuff acquires, by means of an aluminous salt, the properties dependent on alumina, that it can decompose this salt and combine with its alumina, whilst the acid which held it in solution is disengaged and remains in the bath; but we must not thence conclude, that no portion of the acid remains in combination with the stuff, so as to have some influence on the colour. (NOTE B.)

Metallic oxides possess with several colouring particles such an affinity, that they abandon the acids which kept them in solution to precipitate in combination with the colour.

On the other hand, all the oxydes possess the property of combining with animal substances; which several combinations may be formed, by mixing with the metallic solutions an alkali saturated with the animal substance.\*

It is not therefore surprising, that the metallic oxydes can serve as bonds of union between the colouring particles and animal substances; but they differ greatly in this respect. Let us examine on what peculiarities these differences depend.

Although all the oxydes have a disposition to combine with the animal substances, they differ much in this particular; so

\* Mem. de l'Académie, 1784.

that, especially when the animal substances form a solid texture, there are oxydes to which they can hardly unite. Supposing the same degree of affinity, those oxydes which form a stronger combination with the acids ought to abandon them with more difficulty; and again, the same oxyde ought to be more easily precipitated from feeble acids than from such as act with more energy. Hence it is not astonishing that there are only some metallic solutions which can be employed as mordants, and that in conformity with the purpose intended.

Some metallic substances carry into their combinations only a white and colourless base; others modify, by the association of their own colour, and of the colouring matter; but in several oxydes the colour varies according to the proportion of oxygen fixed in them, or according to other undetermined circumstances. The latter oxydes could not serve as a base to durable colours, whose lustre would be easily affected by these ready alteratives, unless it were russet hues, whose slight changes would be imperceptible.

The oxyde of tin surpasses all the others in its property of becoming fixed on woollen and silken stuffs, but especially on the former. It readily abandons the acid which holds it in solution to combine with them, so that it is sufficient to impregnate wool and silk with solution of tin, although they should be then thoroughly washed; a process which does not answer with other metallic solutions.

Tin slightly oxydized, has, in reality, only an ashy colour. But since it has a great affinity for oxygen, it takes enough of it in the ordinary solutions to pass to the white colour; or it may complete its oxydizement even during the operations of dyeing. It retains its oxygen with force, and hence, when highly oxydized, its oxygen exerts but little action on a colouring matter. The oxyde of zinc appears to possess analogous properties, but it has much less affinity with stuffs and with colouring particles; while, on the other hand, it retains the acids more powerfully, and is thereby much less fit for a mordant. (NOTE C.)

The affinity of the oxydes for substances of a vegetable nature appears to be much weaker than for animal substances; whence it happens, that metallic solutions are not well adapted to serve as mordants for colours in cotton and linen. An exception must, however, be made in favour of the oxyde of iron, which

may be applied in a very solid manner to these substances, even when it is precipitated from its solutions. To this purpose Chaptal makes an interesting observation.\* He states, that a solution of iron disturbed by precipitation may be cleared up by moving cotton and linen through it. We must, however, observe, that the oxyde of iron differs in colour according to its state of oxydation; and that the action which it exercises on the colouring substance, varies, as we shall see, according to that state. The oxyde of copper has also some affinity for linen and cotton, so that its solutions may be employed in some processes. Oxyde of manganese announces a similar disposition.

It follows from what we have now stated, 1. That the acids and the alkalies are not fit for mordants, that is to say, for *inter-media* or bonds of union between the stuffs and the colouring substances, although those of sparing solubility can produce species of lakes with colouring matters: 2. That of all the earthy substances, alumina is the one eminently endowed with the properties of a mordant, from its affinity with colouring substances and with stuffs, and from its feeble attraction to acids: 3. That among metallic substances we must distinguish those which afford a white base to the colouring substances, and those which affect the colouring matters by their own colours. Among the former, which are fit for light and splendid colours, the solutions of tin hold the first rank, from the affinity of the oxyde for the stuffs of an animal nature, and for the colouring substances, as also from its weak attachment to acids. The force with which it retains oxygen contributes to its qualities. Among metallic substances, whose colour produces modifications, iron is of the most extensive employment; but its effects vary according to its state of oxydation.

When the colouring particles have precipitated an oxyde from its solvent, the latter has usually the power of dissolving a portion of the combination of the colouring substance with the oxyde, and the liquid remains coloured, although the precipitation be facilitated, and rendered more complete, by the presence of the stuff. The effects depend therefore in part, not only on the proportion, but also on the species, of acid which acts as a solvent to the oxyde. This observation is applicable to acids

\* Mem. de l'instit. tom. iii.

which hold alumina in solution ; but the acids, alkalies, metallic solutions, and even the neutral salts, may serve as alterants.

We observe, that by varying the mordants we may greatly multiply the shades obtainable from any one substance, especially with the co-operation of the alterants. It is sufficient merely to vary the method of applying them. Thus we shall obtain different effects, by impregnating a stuff with the mordant, or by mixing the mordant in the dyeing bath ; by making the operation with heat or cold, with the continued contact of air, or without its intervention ; by means of a solution in a strong acid, or of one in a feebler or more volatile acid.

Drying favours the combination of the bases which have an affinity for the stuff, because the water which produced the solution resists, by its own affinity, the action of the stuff that tends to bring it to the solid state.

But the circumstances by which we ought to be regulated vary according to the qualities of the stuff, which, by a disposition whose cause cannot always be assigned, requires sometimes the aid of heat, whilst a stuff of a different nature combines better in the cold.

Finally, the processes which a stuff should receive in succession, to attain the proposed end, sometimes decide the choice of the solution of the mordant, and the manner of applying it. This is particularly observable in reference to cloths for printing, which should be able to pass through several operations without suffering injury from any one of them.

This beautiful art, (calico printing,) which was introduced into Europe only in the middle of the last century, has made the most rapid progress, having arrived at a perfection not only very superior to the condition in which it has remained for so many centuries in Hindostan, but it has become one whose processes possess the greatest precision, and are susceptible of the most complete explanation.

The perfection to which it has been carried among us, principally by the active and enlightened industry of the celebrated Oberkampf, recently seconded by that of Widmer, is owing in part to the necessity of insulating the processes, in order to succeed, not only in varying the colours and the shades, but likewise in securing to them a permanence which may resist the operations requisite to give due whiteness to the intervals which

separate the printed spots. Hence it has been possible to observe and ascertain the effects of every operation; and hence every colour has been subjected to the severest trials; whereas the other processes of dyeing often confound together different effects, involving them in a fleeting lustre.

Since the processes of this art are well fitted to give an exact idea of the effects of mordants, and of the different circumstances which modify them, we shall here trace an outline of it.

The mordants possessed of great solubility, whose acid, capable of being volatilized, is united to its base by a feeble affinity, are preferred for calico printing, because, as they can be put upon the cloth in a greater state of concentration, and can be more completely decomposed upon it, more intense and substantial colours may be obtained. Their solubility gives them the further advantage of not rendering the mordant clotty, when it is thickened, or unequable during its desiccation on the cloth, by the effect of crystallization.

The acetate of alumina and the acetate of iron possess these properties, and are sufficient to produce, with different colouring substances, the greater number of the diversified hues observable in printed goods.

To prepare the acetate of alumina, three parts by weight of alum, and one of acetate of lead, are dissolved in eight parts of hot water. An eighth part of potash, and as much chalk, are afterwards added. The oxyde of lead contained in the acetate, forms, with the sulphuric acid of the alum, an insoluble salt, which precipitates; while the base of the alum, or the alumina, remains in solution, combined with the acetic acid. Since in this, the generally adopted process, the proportion of acetate of lead, is not sufficiently great to effect the entire decomposition of the alum, the chalk and potash are added, which serve to decompose a portion of this salt, whose crystallization in the inspissated mordant might have rendered its employment prejudicial. We may produce, without the addition of the chalk or potash, an acetate of alumina, which has not this inconvenience, by putting along with the given proportions of alum and water three and a half parts of acetate of lead. (NOTE D.)

The acetate of iron is made by the direct solution of pieces of rusty iron in acetic acid, the *vinegar of commerce*. (The crude

vinegar, called *pyrolignous acid*, is now usually employed for this purpose in Great Britain.—T.)

The mordants are thickened with different kinds of gum, starch, or flour. They should be sufficiently so to preserve, in the impressions of the cloth, the outlines of the objects engraven on the plate, but not so much as to hinder their leaving the plate equably in their application to the cloth. This receives as many different impressions as there are different mordants ; but no more are applied at a time than are to be coloured in the same dyeing bath.

When the cloth is in this condition, it is left for several days, stretched in the workshop, exposed to a moderate heat in a chamber, called in the calico manufactories *the hot room* (or stove). This heat, by favouring the volatilization of the acetic acid, accelerates and completes the decomposition of the mordants, as well as the combination of their bases with the cloth. On coming out of this chamber it is passed into a boiler which contains cow-dung diffused through hot water. The effect of this operation is to dissolve the substance made use of for thickening the mordant, as also the portion of this mordant which, not having combined with the stuff, and being diffused in the dye-bath, would soil it, both by the combination which it would form with the colouring matter, and by the action of the acid which it might deposit upon it. Thus a twofold injury would accrue to the cloth, by the impoverishment of the dye-bath, and by the covering of the portions which should remain white, with the combination, difficultly detachable, of the superfluous mordant with the colouring-matter. Widmer conceives, that there is formed, besides, in the dunging, a triple combination of the animal matter with the alumina and the cloth, which improves the beauty of the colours. This opinion is the more probable, since water alone does not produce the effect of the dunging ; in which process an examination, not however very elaborate, has not enabled us to perceive any other substance capable of acting, except a matter analogous to bile. (NOTE E.)

Before being dyed, the cloths ought still to be carefully washed and beetled, to secure the removal of all the combined mordant. Water and mechanical beating are here employed. (The wash-wheels of our print-fields answer this purpose admirably.—T.) They are then introduced into the dye-bath, where



the whole surface becomes coloured; but the colours are much deeper on the parts impressed with the mordant. The colouring matter thus enters into a triple combination with the mordant and the stuff, thereby acquiring the faculty of resisting external agents much more than when it is insulated or combined with the stuff without any mordant. (NOTE F.)

On this peculiarity are founded the processes employed for restoring, to the parts of the cloth which have received no mordant, the white colour which they possessed before this dyeing. To produce it, the goods are boiled in water along with bran, they are then exposed on the field, observing to lay on the grass the surface of the cloth that bears the colours. By the alternate repetition of these operations, the colouring matters uncombined with the mordants are changed in their composition, dissolved and detached; whereas those which are actually combined, far from suffering change, acquire more lustre, and thus the figures alone remain coloured. (NOTE G.)

This destruction of the colouring particles by exposure in the field, and ebullition with bran, is effected in the same manner as that of the colouring particles of flax, and is explained in the same way. The difference of the process consists solely in the substitution of bran for alkalies; because these would dissolve a portion of the colouring substance fixed by the mordant, and would alter its colour; whereas the bran having a much weaker action on this substance, affects merely the colouring particles, rendered soluble by the action of the air. The identity of the effects of this process with those of common bleaching, has led Widmer to substitute for this method the employment of chlorine, modified by an alkaline solution. Haussman has used this plan with success; and it is known to be practised in many English manufactories.\* (NOTE H.)

From madder, with acetate of alumina more or less diluted with water, are obtained the deep reds, and their different shades, down to a delicate rose colour; with acetate of iron, from black to lilac, passing through all the intermediate violet hues; and finally, with the mixture of these two mordants, in different proportions, the amaranths, the mordores, (brownreds,) the browns, and the puce-coloured. By substituting woad for mad-

\* See Section III.

der, we procure, with the first of the above mordants, the yellows; with the second, only dull olives; but with their different mixtures, we have agreeable olive and bronze colours. Combining the action of these two tinctorial substances in their turn on each of these mordants, very diversified mingled hues are obtained. When we treat of the particular processes of dyeing, we shall enter into more details concerning those which relate to the dyeing of printed goods.

The following are, in general, the steps of the operations of this art. To apply to cloth the most soluble and most easily decomposed mordants; to promote their drying and decomposition; to remove, by animalizing the cloth, whatever has not entered into combination with it; to dye, and to restore to the portions not printed the purest white. To these operations the whole process is reducible. It evidently proves, that linen and cotton are susceptible of combination with the bases of the mordants; that this combination possesses a great affinity for colouring matters; and that it communicates to them the property of being much more unalterable by the ordinary agents of their destruction.

Some colours, however, may be directly printed upon cloth, with all the solidity and lustre of which they are susceptible: such, for example, is that of indigo, known under the name of *pencil blue*, because it is usually applied with this instrument; that called *rust-yellow*, because it is obtained by printing on slightly oxydized oxyde of iron, resulting from the decomposition of two parts of sulphate of iron with one of acetate of lead, diffused in eight parts of water. These are styled *colours of application*. They possess the great advantage of requiring no operations except those of printing and washing. The colours now mentioned, which have been long used, are very durable, and so much the simpler, as they have no need of a mordant; but the number of those possessed of this property are very limited. In others, we must attach to the stuff at the same time, a mordant and a colouring matter, capable of combining together, and of thus uniting with the cloth. This method, analogous to that used for wool and silk, of dyeing in a bath composed of the mordant and the colouring substance, has been hitherto successfully applied in only a very few cases, in consequence of the weak affinity which cotton and linen have for colouring substances united to mordants.

There is another method, still little known, of producing upon cloth, at little expense, a diversity of colours. It consists in applying to the cloth, previously impregnated with the mordants and the dyes, substances which, serving themselves as mordants, modify the shade which the colouring matter has given, with that already existing on the cloth: or to apply some others, which, carrying with them an acid capable of dissolving this mordant, and already combined with a colouring matter, thus substitute a new mordant for that which is on the rest of the cloth, and add also a colouring matter to that which was there before. By a similar process, a white may be induced on dyed goods. Oberkampf formerly employed, and then abandoned this process. Widmer has since improved it much, and applied it to colours which presented the greatest difficulties. The English manufacturers make great use of it; they employ for this purpose a bisulphate of potash, and lemon juice. This composition may answer for cloth which has received little mordant, but it is doubtful if it can serve for others.\* (NOTE I.)

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### CHAPTER III.

#### *Of Astringents in general, and particularly of the Gallic Acid and Tannin.*

ASTRINGENTS deserve peculiar attention, not only because they are of great use in dyeing, but because by this title is distinguished a property common to a great many vegetables.

Perhaps there is no property in vegetables concerning which such vague ideas have been currently received. A slight relation in taste has frequently been deemed enough to rank them in the class of astringents; and every substance has been commonly regarded as astringent or acerb, which turned a solution of iron black. This effect has been presumed to arise from one identical principle residing in all the bodies that produce it. Experience has subsequently shown, that two species of astringents ought to be admitted, viz. tannin and gallic acid. Before describing

\* The principle of Mr. Thompson's patent is excellent for this purpose. Dyed cloth topically impressed with a thickened solution of any vegetable acid, tartaric for example, is passed through a solution of chloride of lime.—T.

the distinctive properties of these two substances, it is proper to consider the gall-nut, which contains them both, the properties of which have been particularly examined, as it is of great use in dyeing.

The gall-nut is an excrescence found on the young branches of the oak, and chiefly of that species called *rouvre*, which grows in the Levant, Istria, and the southern departments of France. This excrescence is produced by the puncture of an insect, which deposits eggs in the small incision which it makes in spring. The juice which exudes from this wound becomes thick, accumulates, and serves as a shelter to the young insect, till such time as it can make its escape. When there is found no outlet for it, it is found dead in the gall-nut. Sometimes, after it has quitted its cell, other insects come to occupy it.

Different kinds of nut-galls are distinguished; some of them are white, others yellow, green, brown, red. Some are of an ash-colour, and even blackish. They vary much in size, and are round or irregular, light or heavy, smooth or covered with tubercles. Such as are small, blackish, granular, and dense, are the best. These are known under the name of Aleppo galls, imported from that town, from Tripoli and Smyrna. In dyeing, galls are usually distinguished into white and black.

Nut-galls dissolve almost entirely by long ebullition in water. Sixteen drams yielded Neumann fourteen drams of extract. Alcohol extracted only four grains from the residuum, which weighed two drams. The same quantity treated at first with alcohol, and then with water, afforded 12 drams and 2 scruples of spirituous extract; the residuum weighed half a scruple more than in the preceding experiment. The spirituous extract has a stronger and more disagreeable taste than the other.\*

Lewis, Macquer, Monnet, and the Academicians of Dijon, made different experiments to determine the properties of the astringent which is contained in nut-galls. They observed, that the black colour afforded with solutions of iron depends on a combination formed between the astringent and the iron. To the suspension of these black molecules, the black colour of ink is owing. If the solution be diluted with much water, these

\* "The Chemical Works of Caspar Neumann, &c." by William Lewis.—From 500 gr. of Aleppo galls Sir H. Davy obtained by aqueous infusion 185 gr. of solid matter, of which 130 was tannin, mucilage 12, gallic acid about 31, calcareous earth and saline matter 12.—T.

molecules fall down under the form of a deep blue powder. It is these which are fixed on cloth dyed black.

We shall, for the present, confine ourselves to these results, because the properties which the astringent presents on different occasions, and in different circumstances, will be better known by an acquaintance with the two substances here included under the same name.

To Scheele the discovery of the gallic acid is due. We shall here introduce the description which this great chemist gave of the method by which he extracted this acid, and of its properties.

“I passed through a coarse sieve one pound of nut-galls, and infused this powder in about six pints of pure water, in a glass globe, leaving it to act for four days, during which it was frequently stirred with a glass rod. I filtered this liquid,\* which was limpid, and which had the colour of French wine. I left it freely exposed to the air, in the same glass globe, covered merely with grey paper. This was done in June. A month afterwards I looked into this infusion, and found it covered with a thick pellicle of mouldiness. In other respects it had formed no precipitate, but it had no longer its former astringent taste, and was more acid. I returned this infusion into the same balloon, covered in the same way with paper. Five weeks thereafter I examined it anew, when it was fully half evaporated: I found a precipitate in it two fingers thick, and at top a mucous pellicle; it had lost all its styptic taste, and it still coloured sulphate of iron black. I filtered the infusion, and left it exposed to the air. By the following autumn the greater part was evaporated away; what remained was mixed with much precipitate. I united these precipitates, and poured cold water upon them. After they had fallen down, I decanted off the water, and then poured on as much hot water as was necessary for their solution. I filtered the whole. The liquid, which was of a yellow-brown, was evaporated at a gentle heat. During the evaporation, one part of it precipitated like a fine sand, and another formed at the bottom in radiated crystals. This salt was grey; and, notwithstanding repeated solutions

\* “If hot water be employed, or if the mixture be digested with heat, the infusion is not limpid: this determined me to employ cold water, and digestion in the cold.”—*Journ. de phys.* 1787.

and crystallizations, it was impossible for me to obtain it whiter.

"This salt of gall-nuts comports itself in the following manner:—

"1. It has an acid taste, causes effervescence with chalk, and colours infusion of litmus red.

"2. An ounce and a half of boiling water is required for dissolving completely half an ounce of this salt; but whenever the solution cools, the whole forms a concrete mass, composed of small crystals. Half an ounce requires twelve ounces of cold water for its solution.

"3. It dissolves very easily in spirit of wine; for half an ounce of this salt, only one-half of boiling spirit is necessary; but if cold spirit of wine be employed, then for half an ounce two ounces of spirit are required.

"4. It readily inflames in a crucible placed in an open fire, melts with the diffusion of an agreeable odour, leaving a charcoal which is difficultly reduced to ashes.

"5. Distilled in a retort, it becomes at first fluid, and affords an acid phlegm. No oil passes over, but at the end a white sublimate rises, which attaches itself to the neck of the retort, and remains fluid as long as it is hot, but afterwards crystallizes. Much charcoal is found in the retort. This sublimate has nearly the smell and the taste of benzoic acid, or salt of benzoin; it dissolves equally in water and in spirit of wine; it reddens infusion of litmus: and what is remarkable, it precipitates metallic solutions with their different colours, and the sulphate of iron black.

"6. The solution of the salt of gall-nut poured into the solution of gold, renders it of a dull green, and eventually throws down a powder which is the gold reduced.

"7. The solution of silver becomes brown, and deposits, with heat, a grey powder, which is reduced silver.

"8. The solution of mercury is precipitated of an orange-yellow.

"9. The solution of copper affords a brown precipitate.

"10. The vitriolic solution of iron becomes black; the stronger the solution, the deeper is the colour.

"11. Lead dissolved in vinegar is precipitated white.

"12. Bismuth gives a precipitate of a lemon-yellow.

"13. Molybdic acid becomes of a dull yellow, without any precipitate taking place.

"14. Platinum, zinc, arsenious acid, tin, cobalt, and manganese, experience no change.

"15. Solutions of lime, magnesia, alumina, and barytes, are not decomposed; but lime water causes an abundant grey precipitate.

"16. The salt of nut-galls is changed into oxalic acid when nitric acid is distilled from it in the usual way.

"The white precipitate obtained when acetate of lead is thrown down by nut-galls, may be again decomposed by sulphuric acid, and the salt of nut-galls is thus obtained in its greatest purity. Since the infusion of nut-galls precipitates the acetate of lead, I thought that I might be able to procure this salt in a manner still more expeditious; but this did not succeed with me, for when I had decomposed this precipitate by means of sulphuric acid, I recovered my infusion of galls with its ordinary astringent taste.

"If gall-nuts be distilled with a violent heat, an acidulous phlegm is obtained, the smell of which is not disagreeable; no oil passes over, but towards the end a volatile salt rises, like that obtained from the salt of gall-nuts distilled, and which has the same properties. (No. 5.) It hence appears, that this salt exists ready formed in the infusion of gall-nuts, although we cannot obtain it in the way of ordinary crystallization, for it is so intimately united with some mucilaginous principle or other matter, that it cannot be separated from it without some interior movement or fermentation."

Before prosecuting the examination of the properties of gallic acid, to which, since the experiments of Scheele, chemists ascribed exclusively the effects of astringents, we ought to describe another substance, tannin, which has some properties in common with it, but differs in other respects.

The art of tanning had been conducted by a blind routine, till Seguin showed that astringents contained a peculiar substance, which, in combining with skin, gave it the properties of tanned leather, and that the tanning effect arose from the combination thus formed. To regulate this art, he had only to determine the circumstances necessary for forming that combi-

nation, and for giving it the requisite qualities.\* He proved that animal glue had the property of forming a similar combination with tannin; for on mingling a solution of strong glue with an astringent infusion, a substance fell down analogous to tanned leather. By this test he could ascertain the quantity and quality of tannin in an astringent substance, so as to trace and measure its effects in the operations of tanning.

Since then, chemists have investigated the means of separating the tannin from the gallic acid. For effecting this object, Proust suggested the muriate of tin, which, whatever be its state of oxydation, is decomposed by tannin, but not by gallic acid. The tannate of tin which falls down, is thereafter decomposed by sulphuretted hydrogen, when the tannin is pure.† But this skilful chemist has himself admitted, that his process was imperfect; for one portion of the tannin remained in solution, while some of the extractive matter accompanied the portion which precipitated.‡

Fielder pretended to separate the gallic acid from the tannin by means of alumina precipitated from its sulphate;§ but on carefully repeating this process, we have observed that the gallic acid combined also with the alumina, and we have not been able to separate it by this method. When gelatin precipitates tannin, the gallic acid, which remains liquid, retains a portion of it; for these two substances exercise a mutual action which opposes their separation, and we have in vain tried different processes for removing this obstacle.

Gallic acid and tannin alike precipitate the solutions of iron. Proust presumes that they cannot combine with the iron, unless it be in the last stage of its oxydation. This opinion has been discussed elsewhere.|| We shall content ourselves with remarking here, that tannin, and especially gallic acid, form with iron a solution of a black-blue colour, as Delaval and Priestley observed with infusion of nut-galls. There is a decomposition of water; but the iron can thus be brought only to the lowest degree of oxydizement. The solution of protoxide of iron in acetic acid, is likewise rendered black by tannin or gallic acid. These facts

\* Journ. de manuf. et arts, tom. iii.; Annal. de chim. tom. xx.

† Annal. de chim. tom. xxv.

‡ Ibid. tom. xli.

§ Journ. de Van. Mons. tom. i.

|| Essais de statique chim. tom. ii.



are sufficient to prove, that if the slightly oxydized sulphate and muriate of iron do not produce a black colour with tannin or gallic acid, this effect depends only on the stronger action which the acids in this case exercise on the protoxide of iron, and Proust himself points out this cause; but whatever happens, it is not the less true, as he thinks, that these metallic salts are of use in dyeing, only in so far as they are highly oxydized; or, that the oxyde of iron absorbs oxygen while it is in the dyeing bath, or during the airing which the stuffs receive on coming out of the bath.

The same chemist has very justly remarked the difference between the precipitates produced by tannin and by gallic acid. "The per-sulphate is precipitated by tannin of a somewhat dirty blue; the deposit is copious, coarse, and black when it is dry. On comparing the precipitate which the sulphate affords with gallic acid, we find that it is very different. The latter is extremely fine, and floats for a long time in the water. It is perfectly black. While the gallate of iron is soluble in acids, the tannate of iron is decomposed by them, parting with its iron while the tanning matter falls."

Lastly, he has observed, that tannin was not a uniform substance; but he regards that obtained from catechu, dragon's blood, sumach, and yellow-wood, as possessing properties sufficiently well marked to form distinct species.

Vauquelin has equally found a difference between the tannin of gum-kino, and that of ordinary tan.\* He remarks, that it precipitates iron of a green hue, like that of cinchona and rhubarb.

This difference among the tannins is very perceptible on making comparative experiments with catechu and gall-nuts, or oak-bark. It may be remarked, even on comparing the precipitates obtained from gelatin, and those astringents whose properties are most similar, such as gall-nuts and sumach. The tannate produced with sumach falls down less readily; it is less friable, and less coloured than that afforded by the gall-nut.

There is such a difference among astringents as to prevent their properties from being considered as identical; there is a like difference among the tannates produced from the different

\* Annal. de chim. tom. xlv.

animal substances and the same kind of tannin; for this property of forming a combination with tannin does not belong exclusively to gelatin. Albumen also possesses it; but the tannates which it forms are much more friable and less coloured than those due to gelatin.

From the preceding statement it appears, that astringents may owe the property of colouring black to the two distinct substances, gallic acid and tannin; and that the latter, far from being identical, has properties which differ more or less in all the vegetables which contain it. One mode of distinguishing substances containing tannin alone, is by examining if the precipitate obtained be readily formed, so as to leave the supernatant liquid colourless. This happens when the tannin of catechu, for example, is precipitated. But if we add a little gallic acid to the solution, the supernatant liquid retains a black colour for a long time. Different astringents examined in this manner, and among the rest oak-bark, appeared to us not to contain gallic acid. Besides gall-nuts, sumach alone exhibited evidence of the acid of galls. That bark must, however, contain but little; for when it is subjected to the process of Scheele, none of it is obtained. But all the astringents afforded with blue test paper marks of acidity, which are even somewhat considerable in catechu, although the presence of gallic acid in it cannot be suspected. Hence, the acidity is not a proof of the existence of the gallic acid, but may be owing to tannin, or a foreign acid.

White gall-nuts, subjected to the process of Scheele, afford pretty soon an abundant deposit, less coloured than that yielded by black gall-nuts. Nor has it the crystalline appearance, though it is the gallic acid which forms this deposit; nor is it in a state of combination. We think it probable that the latter kind of gall-nuts contain a greater quantity of it; though our experiments do not enable us to affirm that this is certainly the case. We have compared the relative quantities of tannin afforded by these two species of gall-nuts, when they are precipitated by gelatin; we have obtained apparently the same quantity of precipitate from both, so that we cannot yet point out wherein that difference consists which distinguishes these gall-nuts, as is observed in the operations of dyeing.

A portion of the gallic acid exists certainly in the gall-nut; but may not some of it be formed in the long space of time

which Scheele's process requires? We are hitherto unable to answer this question; but we are led to suppose, that the tannin is in a great measure destroyed, or that it suffers an alteration which permits the gallic acid, which was in a state of combination with it, to crystallize; for Scheele remarks, that the infusion of gall-nuts loses all its astringent taste. A portion of the tannin is, however, preserved from this change by the action of the gallic acid itself, which retains it in its precipitation and crystallization.

It is this portion of tannin retained by the gallic acid, as obtained by the process of Scheele, which affects its colour, and prevents its properties from being properly insulated. Repeated crystallizations only make it brown, by the decomposition occasioned by the heat. We have tried different methods of purifying this acid; that which succeeded best, consists in treating it with oxyde of tin, newly precipitated from its solution by an acid. The gallic acid then loses its colour, the tannin which altered it being retained by the oxyde, and it crystallizes in very white needles. In this state, it is perfectly similar in its properties to that obtained by sublimation. We have seen that Scheele observed this sublimate, but Deyeux has described it more in detail. He prescribed the precautions which the distillation of the gall-nut requires to obtain this acid sublimate, and he remarked, that one part passed over in the liquor, whilst another was decomposed by the fire. Hence, notwithstanding every care, only a small quantity can thus be obtained. Deyeux supposes, that when this acid is exposed to distillation, as well as its combinations with the oxydes, pure oxygen gas is disengaged, and much charcoal is left behind. But we obtained only carbonic acid during this distillation, which we conducted with the greatest care, with the view of ascertaining the extraordinary result which had been announced.

The oxyde of tin, by means of which gallic acid is purified, appears to retain a portion of it, and to lessen its quantity a little; but we have not observed that decomposition of which Proust speaks,\* probably because it takes place only in the portion combined with the oxyde of tin, of which we neglected the examination; and as he treated the infusion of nut-galls directly

\* *Annal. de chimie*, tom. xlii.

with the oxyde of tin, the quantity of tannin was capable of causing the combination of all the gallic acid associated with it, which does not happen when we thus treat gallic acid retaining but a small portion of tannin.

Gallic acid may also be purified by means of albumen, which, on coagulating with heat, separates the tannin with it; but it retains at the same time gallic acid, and a portion of the albumen remaining liquid along with the gallic acid, causes this to be difficultly separable by crystallization. Hence the first method is preferable.

Gallic acid, in its state of purity, excites an effervescence with the alkaline carbonates, and assumes, on combining with potash and soda, a greenish-blue colour, which becomes so deep by heat, that the liquid appears black at a certain degree of condensation. But it is green if we dilute the liquid, or if we put it into a tube of small diameter. It takes a blue colour with lime, barytes, and strontian; but on adding a greater quantity of acid, the colour becomes red, after passing through several shades. Though it forms precipitates with these alkaline earths, the liquid continues coloured. This acid can scarcely be exposed to ebullition, without assuming a brown shade, and suffering a degree of decomposition.

The observations now presented, concerning the properties of gallic acid, differ from those of Scheele, since, according to him, this acid forms soluble salts with all the alkaline earths, excepting lime water. The reason of which is, that his trials were made with solutions in the acids, so that the acid present did not suffer these naturally insoluble salts to precipitate. We conceive, that this acid forms with all the oxydes insoluble salts, whenever this insolubility is not overcome by the action of an acid or an alkali.

The affinities of tannin appear to differ very little from those of gallic acid, at least in the combinations connected with the art of dyeing. The differences of their effects appear naturally explicable from those of their solubility.

All the species of tannin seem to surpass gallic acid in their tendency to solidity; for, in the first place, they form an insoluble substance with gelatin, while gallic acid remains in a liquid combination with it; but albumen, which has more disposition to coagulate than gelatin, can afford a solid combination with

gallic acid. 2. The combination of tannin with the solutions of iron, forms a precipitate which is speedily separated and deposited, whereas gallic acid produces merely a transparent liquid, whose colouring molecules settle slowly, and only in particular circumstances. 3. Proust has observed, that the alkaline carbonates, and the most part of the very soluble neutral salts, possess the property of precipitating tannin from its solutions, in consequence of the great affinity which they have for water, provided that the proportion of water be not too great.\* Sulphuric acid acts in the same way. 4. The same chemist has observed, and the observation was given in the first edition of these Elements, that when several successive decoctions of gall-nuts are made, the last are destitute of gallic acid.

It is only, indeed, by this superior tendency to form solid combinations, that the properties of tannin appear to differ, in reference to dyeing, from those of several colouring substances, in which it exists in merely a lower degree. Thus the solution of logwood and brazil wood does not form a precipitate with gelatin; but it produces one with albumen when aided by heat. The solution of yellow-wood (fustic) yields a precipitate with gelatin; wherefore it contains a substance analogous to tannin, according to the observations of Chaptal and Proust.† The portion which is not precipitated affords a lighter and livelier yellow; but this portion is itself separated in a concrete form with albumen. On the one hand, several substances employed as astringents have the property of dyeing different shades of fawn and yellow; on the other, the colouring substances which have a deep colour, produce also a black colour with solutions of iron; and the blacks on printed goods are commonly obtained from madder.

The astringents are employed not only to make the baths of the black dye, but also to prepare stuffs by the operation called *galling*, which consists in impregnating the stuffs with the astringent principle of nut-galls, as will be afterwards stated.

It became necessary to determine what part the gallic acid and tannin might each have in this operation. To throw light on this subject, we impregnated with gallic acid specimens of silk, wool, and cotton, and then passed them through a solution

\* Annal. de chim. tom. xxxiv.

† Mem. de l'Institut. tom. ii.

of iron. None of these specimens was coloured black, and the cotton even took no dye; but similar specimens, impregnated in the same manner with infusion of nut-galls, took a black colour with solution of iron. On performing the contrary operation, that is to say, impregnating the stuffs first with solution of iron, we had a similar result. We next ascertained, that by means of tannin, gallic acid also entered into combinations with the stuffs. Hence, in the galling, the stuff unites to both the substances which afford black with the solutions of iron. When the stuff is impregnated with tannin alone, it takes also a black colour. Both the substances associated in gall-nuts contribute therefore to the black dye; while tannin, but not gallic acid, produces an analogous effect when it alone is present. It thence follows, that as both the substances can yield a black precipitate with the sulphate of iron, we may thus judge, at least approximatively, of the effect of the different astringent substances in dyeing black.

A discussion has arisen concerning the properties of oak-bark, which, it was asserted, might be substituted with advantage for the gall-nut, even weight for weight, in all black dyeing. In proof of this it was stated, that oak-bark was substituted in the ordinary proportion for the gall-nuts which the hatters of Paris put into their dyeing baths. But this effect proceeds from the circumstance, that the dyeing of hats is produced particularly by logwood, as we may ascertain by applying to a hat any acid, the muriatic, for example, which reddens it immediately, as happens to all the colours derived from logwood. For this dye, therefore, nothing is required but a very little astringent matter, which seems useful merely to deepen by another shade the colour given by the logwood. In fact, a very small quantity of galls enters into the process commonly employed for hats. We have seen an expert hatter employ only one part of gall-nuts to thirty of logwood.

The present discussion was brought before the Academy of Sciences. The report of its commissioners contains details which may be useful, because they state the proportion of the astringent principle obtained from different substances, and the comparative effect which they produce in dyeing black. For this reason we shall give an extract of it.

The commissioners, Lavoisier, Vandermonde, Fourcroy, and

and the author of these Elements, compared in their experiments, nut-galls, oak-bark, the raspings of the oak taken from the interior of the wood, the raspings of the alburnum, (white bark) of the oak, logwood, and sumach, in order to determine the proportion of the dyeing principle contained in these substances. They took in succession two ounces of each, which they boiled for half an hour in three pounds of water. This first water was followed up by a second, which underwent the same ebullition, and thus they continued till these substances seemed to be exhausted. They mixed together the decoctions which they had obtained. They employed a very clear solution of sulphate of iron, the proportion of sulphate and water in which was exactly determined. They judged first of all of the quantity of the astringent principle, by the quantity of sulphate which each liquor could decompose, and next by the weight of the black precipitate, which was more or less speedily deposited, adding to it a sufficient quantity of water. In order to stop precisely at the point where the addition of the sulphate became superfluous, it was necessary to proceed very slowly with the precipitation towards the end, pouring in the solution of the sulphate only drop by drop, and halting at the moment when a new addition of this substance no longer augmented the intensity of the black colour. When the liquid was too opaque, and when the change of colour could no more be distinguished, a small portion of it was diluted with a good deal of water. To this was added from the end of a glass tube a little of the solution of sulphate of iron, and it was thereby observed if the point of saturation had been attained. Afterwards, when it was wished to make the precipitate fall down in order to be collected, the liquor was diluted with a great deal of water.

This operation deserves attention ; because it is an easy means of determining in dye-houses the just proportions of astringents and solutions of iron ; but we must bear in mind, that the solutions of iron ought to be highly oxydized, in order to produce the greatest effect. Although this consideration was not attended to in the experiments of which we are about to state the results, these merit no less confidence, because the same sulphate of iron was used in all the trials.

To saturate the decoction of two ounces of nut-galls, three drams and sixty-one grains of sulphate of iron were required.

The dry precipitate weighed seven drams and twenty-four grains.

The decoction of oak-bark was of a deep yellow colour. A small quantity of sulphate of iron gave it a dirty reddish hue; a more considerable addition made it pass to a brown-black. Eighteen grains of sulphate of iron were necessary to saturate the decoction of two ounces of this bark. The precipitate collected and dried was in coarser particles and more difficult to divide. It weighed twenty-two grains. The *liber* of the oak presented very nearly the same results.

The decoction of the raspings of the heart of oak required one dram and twenty-four grains of solution, and afforded one dram and twenty-four grains of precipitate. The decoction of the alburnum of oak produced very little precipitate.

The decoction of sumach assumed a violet red colour, when there was added to it a little of the solution of sulphate of iron, of which it required two drams and eighteen grains. The precipitate perfectly resembled that from the nut-galls; but an accident prevented its weight from being ascertained.

The decoction of logwood was coloured sapphire blue by the addition of the sulphate of iron. On exceeding the point of saturation, the blue became greenish and dirty. The quantity necessary to reach the point of saturation, was two drams and twelve grains. The circumstances of colour which we have now mentioned, may differ according to the state of oxydizement.

Trials of dyeing were thereafter made on patterns of woollen cloth. These showed, that the quantities of astringents fitted to give, with an equal weight of the same cloth, a black colour of like intensity, were proportional to the quantities of astringent principle, which had been determined by the experiments on each species; but the black obtained with the different parts of the oak, did not resist boiling so well as that produced with nut-galls.

If the astringents submitted to trial in the preceding experiments, whose results agree with these of Lewis and Beunie, prove that they cannot be compared weight for weight with gall-nuts, and if sumach alone approaches their effects, we must not thence conclude, that they cannot be employed in dyeing black. But we conceive that it would be much more advantageous to make use of them in galling, than in the dyeing bath, because



the black molecules which tannin forms with the oxyde of iron are too quickly insulated and precipitated. We have made a pretty deep black, by treating wool, and even silk, in this manner with oak-bark.

It is said in the "Memoirs of Stockholm" for 1763, that we may substitute for nut-galls *uva ursi*, gathered in autumn and dried with care, so that its leaves continue green.

If gallic acid, the different species of tannin, and several other colouring substances, such as logwood, brazil wood, and madder, afford with the solutions of iron blacks more or less deep, there must be something in common in the mode of acting of these substances, whatever may be in other respects the difference of their properties. It is our present object to determine this.

Monnet, and the academicians of Dijon, formerly remarked, that the solution of gall-nut reduced the metal from the solutions of gold and silver. Scheele observed, that gallic acid produced this effect; and Proust has verified this property, not only in tannin, but also in several other colouring substances. We are warranted to conclude, from these facts, that the astringents, and even the colouring substances in general, possess the property of carrying off oxygen from those substances which can yield it easily.

An observation of Proust informs us, that the astringent produces a similar effect on the solutions of iron. This celebrated chemist evaporated a solution of iron highly oxydized after precipitating it with nut-galls, and he observed that the liquid, after the evaporation, yielded crystals of the green or slightly oxydized sulphate. It thence results, that the black molecules which fall down contain iron in only the lowest degree of oxydation, since they leave in this state even that which they could not abstract from the acid.

The black molecules then contain the iron in a black state (protoxyde.) On the other hand, the astringent, in thus absorbing oxygen, must experience the same changes that it suffers when it is combined with oxygen; but the infusion of an astringent deepens in colour, and becomes brown by simple exposure to air; and we shall see in the following chapter, that it undergoes the same changes which a slight combustion produces, taking this word as signifying a diminution of its oxygen and its hydrogen, so that the carbon becomes predominant.

The astringent ought to experience this effect in a high degree, because it contains a great deal of carbon; for gall-nut leaves, after distillation, more than three-eighths of its weight of charcoal. But when we employ a highly oxydized sulphate, it appears from the experiments of Proust, that a portion of the tannin is altered in its nature by a too energetic action of the oxygen.

We see now, how the black molecules may result from a combination formed of black oxyde of iron and a substance which must assume by degrees the same colour; why astringents, although differing in their other properties, ought to produce an analogous effect; and finally, why colouring substances of very different kinds afford, with solutions of iron, colours approaching more or less to the black hue.

We may observe that the gallic acid exhibits in its action on solutions of iron a small difference, which seems to announce, that it possesses in a less degree the property of abstracting oxygen from iron. Tannin produces a black colour in a sulphate, so little oxydized that the gallic acid does not change its hue, unless it remains exposed to the air.

On comparing all the observations advanced on astringents, we may draw the following conclusions:—

1. Gallic acid cannot serve by itself for the black dye, but it may contribute to the effect caused by the tannin, either by combining with the stuff, or by becoming fixed in the dyeing bath on the galled stuff.

2. Tannin may serve, without the aid of gallic acid, for the black dye. The different species of tannin possess in this respect different properties as to the quality of the black, which can be determined only by direct experiments. Astringents, besides the quality of the black which they afford, differ also in the quantity. Thus oak-bark, and the other parts of this wood, contain far less astringent matter than gall-nuts.

3. It is especially for the galling that those astringents which do not contain gallic acid may replace the gall-nuts, because the black molecules which these form fall down too slowly; and besides, the quantity which must be employed to replace the gall-nuts would be too considerable, and would embarrass the dye-bath. Sumach is, among the astringents at present known, the one which approaches the most to gall-nuts, and which is the fittest to replace them.

4. With regard to ink, in which the colouring particles must not precipitate, no known astringent can be substituted for gall-nuts, not even sumach, as Lewis has proved in his excellent observations on this preparation, which deserve to be somewhat dwelt upon.\*

If too large a portion of sulphate of iron be added to the galls, the ink becomes speedily brown, and then passes to yellow, because the astringent is destroyed by the action of the oxygen which the sulphate of iron affords, or progressively attracts from the atmosphere; for we shall see, that oxygen eventually destroys those colouring substances with which it is combined in too great quantity. When this accident happens from age, Lewis found, that an infusion of gall-nuts passed over the altered characters restored them; and Blagden has indicated a means still more efficacious, which is the prussiate of an alkali.† Lewis ascertained, that the best proportion for ink was three parts of gall-nuts to one of sulphate of iron; that cherry gum and plum-tree gum were as good as gum arabic for giving the necessary consistence, and for keeping suspended the black molecules which tend to fall; and that decoction of logwood, employed instead of water for the infusion of the gall-nuts, improved the beauty of the ink.

We have remarked, that both gallic acid and tannin gave to iron the property of decomposing water, and of forming by this means a solution of iron, which passes from blue or violet to black. Delaval says, that he produced with the solution of this metal and an infusion of nut-galls, the deepest black, and the most indelible ink.‡ He adds, that on plunging into this tincture silks and woollen stuffs, without adding any acid to it, he obtained them of the deepest and most indestructible black colour. Proust also says, that he would prefer, both as to durability and beauty, the ink made by dissolving iron in an infusion of gall-nuts, to that which is prepared with the sulphate of iron.§ He remarks in the same place, that the combination of gallic acid and tannin with iron, is not changed into prussiate of iron by the prussiate of potash; an observation which had already been made by the academicians of Dijon.

\* Lewis's Exper. Essay on the Commerce of the Arts.

† A solution of ferropussiate of potash, faintly acidulated, or sulphuretted hydrogen water, are the best restoratives of the characters of faded ink.—T.

‡ Experimental Inquiries.

§ Ann. de chim. tom. xxxv.

We have already mentioned, that Lewis had observed that a decoction of logwood increased the beauty of ink. It is observed, especially in the black dyes, that an addition of logwood gives more lustre to black; and we shall see, that it is advantageous to fix a blue colour on stuff which is to be dyed black. Now, logwood forms with the oxyde of copper, added to black dyes, a blue colour, which contributes to the beauty of the black by the mixture of that hue.

We must here remark, that the black of the dyes is produced only by the condensation of the molecules, which when more diffused enjoy a particular colour, such as blue, dun, or violet. But the mixture of two substances, whose diluted colour is different, yields a more intense black. This effect is readily observable in the mixture of two liquids of a deep colour, even when no precipitation occurs by their mutual action. On this occasion we shall adduce an observation of Hooke, quoted by Newton: "If we take two coloured liquids, the one red, the other blue, in sufficient quantity for them to appear very dark, although each part be pretty diaphanous, they will cease to be so on their mixture; for the one transmitting only red rays, and the other transmitting only blue rays, none will any longer pass through the two liquids mixed together."\*

The result is not, however, exactly such as Newton states it, provided the two liquids are not of a nature to produce a precipitate. The colour transmitted is always different from the two insulated colours, and always deeper; but if the mixture appears opaque in a vessel of a certain size, it will appear still transparent in a vessel of a smaller diameter.

We perceive, therefore, that it must be advantageous, for obtaining an intense black, to mingle different astringents, the black of which is derived from different colours. Perhaps gallic acid may thereby augment the black occasioned by the tannin; and perhaps it would be beneficial to employ a mixture of different kinds of tannin in galling.

We have hitherto considered tannin only in reference to black dyes; but its use is not confined to this kind of dyeing: it exerts on several other colouring particles an affinity analogous to what we have observed between it and gallic acid; whence it serves to fix them on stuffs, and to communicate stability to them.

\* Optics, vol. i.

In this point of view it may be compared to mordants; but as it possesses in itself a colour which has a tinge of yellow or dun, and as the effect of one colour must be to modify and darken that peculiar to another colouring substance, the use of astringents as a mordant does not suit bright colours, particularly those of little intensity.

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#### CHAPTER IV.

*Of the action of different Substances, particularly of Air and Light, on Colours.*

HITHERTO we have considered the colouring molecules only as substances forming different combinations, by which their properties are modified; but they may yield more or less easily to the action of other substances, which destroy the combination thus formed, or which by a sur-composition deteriorate their properties. They may suffer the alterations produced by external agents, either from the mutual action of their principles, or of the substances which form a combination with them.

The power of resisting vegetable acids, alkalies, soap, and above all, the action of air and light, constitutes the durability of a colour; but this property has a very unequal standard, according to the nature of the colour and the species of stuff; for in certain silk dyes the same permanence is not required as in those of wool.

There is no obscurity in the action of water, alkalies, acids, and soap: a solution is effected by means of these agents, or a small portion of acid or alkali unites to the combination which forms the colour; for this is not destroyed, but merely changed, and can be restored by removing the acid or the alkali.

This is not the case with the action of air and light. Till lately, it was not known in what this action consisted; but we are at the present day much farther advanced in this theory, which we proceed to detail.

Scheele had observed, that oxygenated muriatic acid (chlorine) rendered the vegetable colours yellow, and he ascribed this effect to the property which it possesses, of seizing the phlogiston which enters into their composition.

The author of the *Elements* proved,\* that the properties of oxygenated muriatic acid (chlorine) arose from the oxygen, which it readily yielded to the substances exposed to its action; that it commonly brought the colouring particles to a yellow hue; but that, by a continuance of its action, it destroyed their colour, though he did not determine wherein this action consisted.†

With regard to the action exercised by oxygen on the colouring particles, Fourcroy afterwards made several observations which throw much light on the changes which they experience, especially when their aqueous solution remains exposed to the air, or when it undergoes ebullition. He remarked that, by the action of the air, vegetable decoctions formed pellicles, which lost their solubility, and progressively changed their colour. He traced the gradations of colour thus obtained, and concluded from his observations, that oxygen entered into the composition of these colouring particles; that when it combined with them their hue changed; that the more of it they absorbed, the more fixed their colour became; and, that the mode of procuring unchangeable colours for painting was, to select those which had been exposed to the action of chlorine.‡

The author of these *Elements* sought to determine more peculiarly wherein the action of the air consisted, when it combines with the colouring particles, especially by examining the operation of chlorine upon them.§

We shall copy literally what had been stated in the first edition of these *Elements*, because Bancroft, whose authority has great weight with us, has attempted to refute the theory there established, and because we are desirous of enabling our readers to weigh his reasons, and the grounds of our opinion.

“We must distinguish, in reference to the effects of the air, between the colours of metallic oxydes and those of the colouring particles. I have proved, that the modifications of the former are owing entirely to the different proportions of oxygen; but I have been led by my observations to a different opinion concerning the modifications of the other colouring particles.

\* *Mem. de l'acad.* 1785.

† For the theory of blanching by chlorine, see Note § to page 38.—T.

‡ *Annal. de chimie*, tom. v.

§ *Annal. de chimie*, tom. vi    *Mem. sur l'action que l'acide muriatique oxygéné exerce sur les parties colorantes.*

“ I have observed, that chlorine exhibited different phenomena with the colouring particles ; that sometimes it discharged their colour, rendering them white: that more frequently it caused them to become yellow, dun, brown, and black, according to the intensity of its action ; and that, when their colour seemed to be discharged or blanced, heat, or the lapse of time, was sufficient to render them yellow.

“ I have compared the effect produced by chlorine, when the colouring particles are rendered yellow, fawn or brown, with the effects of a slight combustion ; and I have shown that they were identical, that they were owing to the destruction of the hydrogen, which, combining with oxygen more easily, and at a lower temperature than charcoal, leaves this predominant, whence the natural colour of charcoal is blended more or less with that which pre-existed.

“ This effect is very perceptible, when sugar, indigo, or the infusion of nut-galls or of sumach, is submitted to the action of chlorine. The sugar and indigo assume a deep colour, and afford unequivocal traces of a slight combustion. The infusion of gall-nuts and of sumach forms a black deposite, which is charcoal nearly pure.”

These phenomena are analogous to those observed in the distillation of an organic substance. In proportion as its hydrogen is disengaged under the form of oil, or in the state of gas, the substance turns yellow, and eventually only a black charcoal remains. If we expel the hydrogen of an oil by heat, it becomes brown.

Other experiments which I have made on alcohol and ether have satisfied me, that oxygen united to muriatic acid possessed the property of combining with the hydrogen, which abounds in these substances, so as to form water.

When, therefore, chlorine renders a colour yellow, dun, or brown, this effect is caused by the colouring substance suffering a slight combustion, in which a greater or less part of its hydrogen has formed water ; whence the carbon becoming predominant, communicates its peculiar colour.

I have shown, that the art of bleaching goods depended on this alteration of the colouring particles by the oxygen of the atmosphere, the dew, and chlorine. The colouring particles of flax become soluble in the alkali of the leys, which must be

alternated with the action of the oxygen. We may afterwards precipitate from the alkali these colouring particles, which when dried and collected are black. They therefore prove the truth of this theory, both by the colour they have assumed, and by the quantity of carbon they afford in their analysis.

“The alkaline solution of the colouring particles of the cloth, which is blackish-brown, loses nearly its whole colour on pouring into it a quantity of chlorine; and the same effect may be observed with several other substances, which have derived a colour from a commencement of combustion.

“A cloth may appear white, and yet become yellow in process of time, especially if it be exposed to certain degrees of heat, when the oxygenized particles have not been removed by a sufficiently efficacious ley. In like manner, the green particles of vegetables are blanched by the chlorine, but become yellow on ebullition.

“These facts prove, that oxygen may whiten or render pale the colouring particles with which it combines, whether it has begun to produce on them the effects of combustion, or whether it may produce these effects but slowly, and especially when this combustion is subjected to a certain degree of heat.

“It is very probable that, in every case, one portion of the oxygen unites with the colouring particles without combining particularly with the hydrogen, and that thereby the colouring particles of the flax have become, from the action of the oxygen, more soluble in the alkalies than they previously were.

“The action of oxygen has an undoubted influence, in several other circumstances, on the changes effected in the colouring particles of vegetables. These particles are formed chiefly in the leaves, the flowers, and the inner bark of trees. By degrees they experience a slight combustion, either by the action of the atmospheric air which surrounds them, or by that of the air carried into the interior of the vegetables by particular vessels; whence it happens that the most part of trees contain colouring particles of a dun hue, verging more or less on yellow, red, or brown, which, by means of this combustion, thicken, and are eventually thrown out of the vascular fibres of the bark, of which I have found them to form the greater proportion.

“These observations teach us in what manner the air acts on colouring substances of an animal or vegetable nature: it first



combines with them, making them weaker and paler, and gradually establishes a slight combustion, by which the hydrogen in their composition is destroyed; they pass to yellow, russet, dun; their affinity with the stuff seems to diminish, they are detached from it, they are carried off by the water; and all these effects vary, and are finished more or less quickly, and more or less completely, according to the nature of the colouring particles, or rather according to the properties which they possess in their actual state of combination.

“The changes which occur in colours, arising from the combination of the colouring particles with the metallic oxydes, are a compound effect of the change produced in the colouring particles and the metallic oxyde.

“The light of the sun accelerates greatly the destruction of colours; it ought then (if the theory which I have laid down be just) to favour the combination of the oxygen, and the combustion thereby produced.

“Sennebier has given a great number of interesting observations, concerning the effects which light occasions in the different substances, and particularly in colours; he ascribes these effects to a direct combination of the light with these substances.”\*

The influence of light on the colour of woods has been long ago remarked. In obscurity, they retain their natural state; but when exposed to light, become yellow, brown, and pass into other shades. Sennebier observed the differences exhibited by several species of wood in this respect. He found that the changes were proportional to the vivacity of the light; that they took place even under water; that moistened woods, however, suffered changes less rapidly than those which were dry; that it required several folds of ribbon to preserve a wood entirely; that black paper was sufficient, but with paper of other colours the alteration was not prevented. A simple envelope of white paper was insufficient, but two intercepted the action of the light.

“This skilful philosopher extended his experiments to a great

\* “*Mem. physico chimique sur l'influence de la lumière solaire,*” &c. tomes ii. et iii. This philosopher, to whom physics is under so many obligations, has adopted, in a great measure, (*Physiol. veget. tom. v.*) the ideas exposed here; and among which we must distinguish between the positive consequences of observation, and the applications that are yet merely conjectural.

number of vegetable substances. They may serve to clear up several phenomena of vegetation, with which I have at present no concern. But to prove wherein the action of the sun on colours consists, it would be sufficient to examine the phenomena exhibited by the solution of the green particles of vegetables in alcohol.

"If this solution, which is of a fine green colour, be exposed to the light of the sun, it speedily takes an olive tint, and then is discharged in some minutes. If the light has little vivacity, the effect is much slower; but in perfect darkness, the colour is preserved without alteration, or at least the alteration is very tardy. Sennebier says that an alkali restores the green colour; but if the liquid has experienced all the discoloration which it can undergo, the alkali produces no change on it. He remarked, that in azote or nitrogen the colour was not affected, and that it suffered no change if the flask was full.

"I inverted over mercury a flask half filled with the green solution, and exposed it to the light of the sun. When the colour was discharged, the mercury was found to have risen in the flask, and consequently the vital air had been absorbed, the oxygen having combined with the colouring particles. I have not observed the deposite of which Sennebier speaks; the liquid remained transparent, and of a clear yellow colour.

"I evaporated this liquor; its colour soon deepened, becoming brown; and the residuum was black, and in a carbonaceous state.

"The light acted therefore by favouring the absorption of oxygen and the combustion of the colouring matter. At first, the marks of the combustion are not perceptible, the liquid preserving merely a feeble yellow colour; but the combustion is soon consummated by the action of the heat, when the liquid turns brown, and leaves a black residuum. If the vessel in which the liquid is put contains no oxygen gas, the light has no action on the colouring particles. The azotic gas suffers no diminution.

"The circumstance of ribbons and a simple white paper not protecting from the action of light merits attention. It can penetrate through envelopes which appear to us opaque, so as to exert its energy at greater or less depths.

"Beccaria, and after him Sennebier, have compared the

effects which light produces on ribbons of different colours ; but the differences which they observed ought to be ascribed to the nature of the colouring substances with which the ribbons were dyed, rather than to the colours themselves ; for a ribbon dyed with brazil wood will lose its colour much more speedily than one dyed with cochineal, though the shade be the same.

“Although light greatly accelerates the combustion of the colouring particles, and though its presence even appears necessary for the destruction of some of them, yet this effect takes place in other circumstances without the aid of light. Having placed several plants in darkness, in contact with oxygen gas, I observed that some of them absorbed it. I also observed, that the rose changed and took a darker tint without the contact of the air, undoubtedly because it contains a little oxygen, whose state of combination becomes afterwards more intimate ; but several species of flowers preserved their colour perfectly well in azote.

“I placed tincture of litmus in contact with oxygen over mercury, in darkness, and in the sun-light : the first was preserved very long without alteration, while the gas experienced no diminution ; the second lost much of its colour, it became red, the oxygen gas was in a great measure absorbed, and a little carbonic acid was formed, which undoubtedly produced the change of the blue colour into red.

“This observation may give some idea of the changes of colours occasioned by a peculiar disposition of the principles existing in a vegetable substance, when it experiences, by combination with oxygen, the effects of a slight combustion, which may generate some acid, as in the leaves which redden in autumn previous to their turning yellow, and in the streaks observable in flowers of languid vegetation.

“It is therefore proved, that light promotes the absorption of oxygen by the colouring particles, and that a combustion thus takes place, the ordinary effect of which is a predominance of carbonaceous particles.

“To the same cause must be ascribed the decay remarked in stuffs themselves by the action of light. ‘Among several examples which I might adduce,’ says Dufay, ‘I shall mention only a curtain of fugitive crimson taffeta, which had remained long stretched behind a window : all the parts which were

opposite the panes of glass were entirely deprived of colour, whilst those which corresponded to the wood of the casement were much less faded; and further, the silk itself was almost destroyed in the discoloured parts, where the curtain could be torn with the slightest effort, whilst it retained elsewhere nearly its usual strength.\*

“The colouring substances resist, therefore, the action of the air in a greater or less degree, according as they are more or less disposed to combine with oxygen, and to suffer from its action a combustion more or less speedy, more or less considerable. Light favours this effect in several circumstances; its concurrence is essential; but the insulated colouring particles are much more subject to this combustion than when they are combined with a substance such as alumina, whether this defends them by its incombustibility, or whether the force of affinity binds them up, so to speak, and enfeebles their action on other substances; and in this principally consists the utility of mordants. Finally, the latter combination acquires still greater unchangeableness when it is intimately united with the stuff.

“Thus the colouring matter of cochineal is easily dissolved in water, and its colour is quickly affected in the air. When combined with the oxyde of tin, it is much more lively, and scarcely soluble in water; but it is still readily altered by the air and by chlorine. When it exists in triple combination with woollen stuff, it resists these agents better.

“From these observations we are not to conclude that all the yellow colours proceed from the carbonaceous portion of the colouring substances; different compositions may afford the same colour. Thus indigo is entirely different from the blue of our flowers, from the blue of oxyde of copper, and from prussian blue.

“Nor do I assert that oxygen may not unite in a small proportion with some colouring particles, without weakening their colour, or changing it to yellow. We shall find in the chapter on indigo, that this substance possesses a green colour when combined with an alkali, lime, or a metallic oxyde; but that it resumes its colour, and separates from these solvents, on re-

\* Mem. de l'academie, 1737.

covering a small portion of the oxygen which it had lost. The liquor of the *buccinum*, which served for dyeing purple, is naturally yellowish; on being exposed to the air, and particularly to the sun, it passes speedily through different shades, and finally assumes that colour which was deemed so precious by the ancients.\*

“It may be regarded even as a general fact, that colours assume more brilliancy by combining with a small portion of oxygen. It thence happens that the stuffs, as they come out of the bath, ought to be agitated in the air, and sometimes withdrawn from the bath at intervals, in order to expose them to the atmosphere. But the quantity of oxygen which fixes itself, thus contributing to the lustre of the colour, is very inconsiderable in some cases, and the degradation of shade soon begins.

“The action of the air affects not only the colouring particles and the stuff, but also the metallic oxydes which serve as an intermedium to them; because the oxydes, which are at first deprived of a portion of their oxygen by the colouring particles, may recover some of it. Hence, the oxydes, whose colour varies with the proportion of their oxygen, exert an influence on the changes experienced by the stuff. The alteration of the colouring particles must also contribute to this effect.

“I have stated, that the colouring particles, in a state of combination, were less liable to be affected by the action of the air than when they are insulated. This is a circumstance very commonly observed. There are, however, particular exceptions. Alkali produces a contrary effect. I half filled a phial with an infusion of cochineal, and exposed it to light over mercury; another phial, similarly situated, contained an infusion of cochineal made with a little tartar; and in a third, some alkali was added to the infusion. The second phial suffered least alteration in the same space of time, accompanied with the least absorption of air.

“In the third, the liquid became at first brown, then the colour disappeared, and the absorption of the air, although inconsiderable, was greater than in the two others. By evapora-

\* “Decouverte d’une nouvelle teinture de pourpre, &c. par Reaumur; Mem. de l’academie, 1711.” According to the testimony of Eudocia, the purple took its lustre, and arrived at its perfection, only by exposure to the sunbeams.

tion it assumed a brown colour, and the residuum was yellow-brown.

"I have made similar experiments on several colouring substances: the alkali deepened their colour, which grew more and more brown; and it likewise favoured the absorption of the air. Madder alone seemed to form an exception; its colour, which at first became deeper, was more durable than that of the infusion without alkali.

"The usual effect of alkalies on colouring particles is conformable to what they produce on several other substances, such as sulphur. They promote the absorption of the air, because they have a strong affinity for the substance which results from this absorption.

"From this operation of alkalies, I explain a fact observed by M. Becker.\* When alkalies have rendered a vegetable infusion green, we see it pass by degrees to yellow, if it be left exposed to the air; and when the yellow is once established, acids can no more bring back the primitive colour. But this effect does not occur when we abandon in the same way, for some time, a vegetable colour which has been turned red by an acid. We must, however, except those acids which act by giving up their oxygen; for the colour is equally destroyed in that case."

Bancroft advances, in opposition to what we have thus stated: 1. That the colouring substances experience, from the action of acids and other bodies, an alteration which cannot be compared to combustion. In the preceding explanations, however, the question is merely about the kind of alteration which depends on the action of oxygen.

2. That oxygen, far from destroying colours, is sometimes necessary to them; for example, to indigo. Is not this what we have said? But we distinguish between the cases where it becomes an element of the colour, and those where its action is destructive.

3. That the changes of colours produced by the air cannot be ascribed to the carbon, which becomes predominant, because several substances contain much carbon without having a colour similar to what is ascribed to its excess, and because the colour of carbon itself is due to oxygenation.

\* Specimen, &c.

We have attempted to demonstrate, that the changes produced by the air when its action is favoured by light, are especially owing to a combination of the hydrogen of the colouring substance with oxygen, whether this be absorbed from the atmosphere, or be present in less intimate combination, either in the colouring substance itself, or in the oxyde united with it; and that the effect was similar to a slow combustion, in which a combination of hydrogen with oxygen was formed, so as to leave a residuum containing a redundancy of carbon. This opinion seems to be an immediate consequence of the phenomena that have been detailed, which indicate the gradual decomposition of all bodies containing hydrogen on being subjected to this action of oxygen.

Bancroft regards charcoal as an oxyde, which he compares to the oxyde of manganese. We do not think it necessary to take up time in refuting his opinion\* concerning the nature of charcoal. The only object is to know, if, in the circumstances under discussion, the change of colour may not have some analogy with what is observed when a vegetable substance is distilled. He pretends that this substance becomes in that case brown, merely by the accession of oxygen from the atmosphere. Let a distillation be made out of contact of the atmospheric air, and he will observe that the same alteration of colour takes place, either from the formation of water, or from the disengagement of a greater proportion of hydrogen, so that the properties of the charcoal become predominant.

Bancroft maintains, that the theory which he combats is founded only on the phenomena of the colouring particles of the cloth. The text which we have adduced proves the contrary, and we might easily multiply examples.

It was incorrect, according to him, to confound the effects of the combination of oxygen gas with those of the chlorine; but we do not find in his work the experiments which he announced as calculated to prove, that the chlorine often produces effects contrary to those arising from the combination of oxygen.

We ought, undoubtedly, in comparing the effects of chlorine with those of the absorption of oxygen gas, to take into consideration the greater condensation of oxygen in the former,

\* *Essai de statique chimique*, tom. ii.

and the natural effects of muriatic acid.\* We should also distinguish between the effects which the chlorine can produce, when it has made the whole colour disappear, as we have seen, and the effects due to the combination of its oxygen with the hydrogen of the colouring particles, as well as those arising from the difference of the colours, of which we shall speak in the sequel.

The more lively oxygenation, by means of chlorine, prevents us from obtaining readily those gradations of colour which are produced by the action of the air, and which become more difficult the further they advance. Thus, conformably to the observation of Fourcroy, when a colouring substance has experienced some change by this action, it becomes, in similar circumstances, more fixed; but in this first effect, a part of its hydrogen must have entered into combination.

While we conceive that we have been able to refute the objections of Bancroft concerning at least the most usual cause of the degradation of colours by air and light, we admit, that the consequences of the opinion which we endeavour to maintain, should not have been extended to the phenomena that we are now going to examine, although this has been done with much diffidence, and without overstepping the limits of a simple conjecture.

Nitric acid, chlorine, and sulphurous acid, exercise on animal substances a peculiar action, which merits examination, because it may furnish some processes to dyeing.

Brunwiser† having observed that woods assumed different colours on exposure to air, sought to determine the origin of these colours, and to produce them artificially. He remarked, that on moistening with nitric acid the surface of wood, principally young wood not very dry, it took a yellow colour. On performing the same operation with muriatic acid, and sulphuric acid, the wood assumed a violet colour; and he looked upon this violet as composed of a blue and a red colour. From these observations he concluded, that as all the colours are produced

\* Translating M. Berthollet's idea into the modern language of chemistry, we would say, "Take into consideration the intense affinity of chlorine for hydrogen, the liberation of oxygen from the decomposed water, and the peculiar action of muriatic acid."

† Versuche mit mineralischen sauern Geistern, aus den holzern Farben zu ziehen, 1770. In Abhandlungen der Baierischen Akademie.



by the mixture of yellow, blue, and red, those which we observe in the leaves, fruits, and flowers, arise from the colouring particles which exist in the wood, but which are disguised by an alkali; that the mineral acids, on seizing this alkali, set the colouring particles at liberty; and that the fixed air, in penetrating into the leaves, the fruits, and the flowers, naturally produced the same effect, by combining with the alkali which masked them.

The author attempted to apply to the arts his pretended discovery as follows.\* After watering chips of wood with nitric acid, he poured water upon them, filtered the liquid, and made use of it to dye wool, silk, and goat's hair, of a durable yellow; a colour due, by his account, to the yellow particles which were contained in the wood, and which had been extracted or set at liberty by the nitric acid.

De la Folie relates,† that having plunged a skein of white silk into nitric acid, or aquafortis, of the usual commercial strength, the silk assumed in three or four minutes a fine jonquil-yellow hue. He washed it repeatedly with water, that no adhering acid might remain to alter it. This colour resisted several tests to which he exposed it, and the silk retained its primitive lustre. When dipped into an alkaline solution, it takes a beautiful orange colour.

Several experiments on this process are to be found in a dissertation published by Gmelin.‡ He says, that he has given a fine sulphur colour to silk by keeping it for a day in cold nitric acid, or for a few hours when the acid was hot. Ebullition with soap and water impaired the lustre of this colour. It became of a fine lemon colour by keeping the silk for twelve hours in an alkaline solution; and it assumed a fine gold hue when this solution was hot.

All solutions of metals in nitric acid gave to silk a yellow colour more or less deep, as well as the solution of alumina in the same acid. But the solution of calcareous earth and of magnesia produced no effect.

\* Entdeckung verschiedener vegetabilischen farbematerialien seiden und wollen zeuge schon und dauerhaft gelb zu Farben, 1771.

† Journ. de Phys. tom. iv. p. 349.

‡ J. Frieder. Gmelin, Prof. Götting. de tingendo per nitri acidum, sive nudum, sive terra aut metallo saturatum serico. Erfurti, 1785.

The solution of tin mixed with solution of gold yielded, according to La Folie,\* a purple colour, which fixes upon silk; but Gmelin obtained by this process only a common yellow. He proves also, that the different yellows which Struve said he had obtained from different metallic solutions, depend merely on the acid of these solutions.† The only exception, perhaps, is the solution of mercury, which gave silk a copper colour.

Baumé describes a process capable of protecting silk from any alteration.‡ “A mixture of two drams of nitrous acid and one pound of alcohol is made, into which a few ounces of manufactured silk are put, either yellow, or previously whitened, for that is absolutely indifferent. The vessel containing them is placed for about 24 hours in a water-bath heated to 30 or 40 degrees R. (100° or 120° Fahr.) The silk becomes of a dull yellowish-brown. It is now repeatedly washed in water, to remove the acid with which it was impregnated. It is then scoured with soap in the usual way; afterwards washed to free it from the soap water, and finally dried.

“If we view this silk in the sun, it shines like threads of gold. By the same process we may give silk different shades of the above colour, and form what is called in dyeing *degradation* of colour from white to the full tint. For this purpose it is sufficient to let the silk infuse for a shorter time; the first shade is procured by one hour's infusion, and the others in proportion to their duration.”

Bergmann was aware of this process, when he published his notes on the Treatise of Scheffer.§ He says, that ordinary aquafortis gives, in three or four minutes, to wool and silk, a bright, fine, and durable yellow; that they must be immediately washed; and the more dephlogisticated the acid (the more colourless), the greater effect it produces.

To recapitulate: nitric acid, diluted with a certain quantity of water, gives silk a yellow colour, of more or less depth, according to the concentration of the acid, the temperature, and the time of immersion: the silk must be carefully washed on coming out of the acid. This colour has a good deal of lustre. We may

\* Journ. de physique, tom. viii.

† Bernerisches Magazin der Naturkunst und Wissenschaften, vol. i.

‡ Ann. de chimie, tom. xvii.

§ Essai sur l'art de la teinture.

deepen the shade without perceptibly affecting the silk. This process may be usefully applied, not only to silk, but to other animal substances; and the colour may be modified by alkalies.

The solution (nitric) of calcareous earth, and that of magnesia, produce no effect on silk, because they do not retain an excess of acid. Solutions of alumina, and of all the metallic substances, produce on the contrary a yellow of greater or less depth, because they all retain a greater or less excess of acid; and it is the acid in excess which acts on the silk as free acid. It was the acid alone which coloured the animal substances yellow, in the experiments of Brunwiser, and not the extracts of the wood.

The yellow colour is not owing to iron, as De la Folie pretended; for the purest nitric acid, which consequently contains no iron, produces it as well as that in which the presence of a little of this metal may be suspected.

If silk be put into concentrated nitric acid, it speedily takes a deep yellow colour, loses its force of cohesion, and is dissolved. During this solution, the azote which enters into the composition of animal substances is disengaged, occasioning a long effervescence.\* If heat be applied, much nitrous gas is formed, and the liquid at first assumes a dark colour, becoming brown. At this period, the oxygen of the nitric acid combines particularly with the hydrogen which abounds in animal substances, serving to form the oil extracted by distillation, which renders them so combustible. One part of the oxygen enters into a new combination, forming oxalic acid; but, at the same time, another substance of a detonating quality is produced, which is yellow and bitter, whence it has been called *amer* by Welter.†

Welter extracted this substance not only from silk, but from other animal substances; and he observed, that it communicated to white silk a beautiful yellow, which washing with water did not impair.

It is to be desired that this expert chemist had prosecuted his trials, in order to determine more exactly both the nature of this substance and the circumstances of its production; we might perhaps be able to deduce from it the cause of the yellow colour which nitric acid communicates to animal substances

\* Mem. de l'acad. 1785.

† Ann. de chimie, tom. xxix.

when the action of this acid is less lively than that just described. Perhaps, when it is confined to the surface of the silk, the formation of this substance on it is determined by the tendency of the silk to combination.

Chlorine gives likewise a yellow colour to animal substances ; but this does not seem to be a general effect. We have seen skins bleached by chlorine, and this colour is always much more intense than that owing to nitric acid : thus, it appears to differ from it, and to arise merely from a feeble combination of the oxygen with the animal substance, which, when it is white, takes a nearly similar hue on long exposure to the atmosphere. It is also to be remarked, that the action of chlorine weakens animal substances more easily than nitric acid, although the latter be more condensed.

Sulphurous acid exercises also a peculiar action, which deserves more consideration, as it enters into the practice of dyeing.

According to the observation of De la Folie, roses blanched by the vapour of burning sulphur, become green in an alkaline ley, and red in the acids. Sulphurous acid reddens tincture of litmus, which possesses a very fugitive colour ; but it acts just like the other acids on infusions of yellow wood, brazil wood, and logwood ; its vapour, however, is much more active, in which respect it resembles chlorine.\* Hence it is not judicious to substitute the use of this for the fumes of sulphur.

When silk has undergone the action of the sulphur which is to complete its whitening, sulphuric acid disengages from it an odour of sulphurous acid, although this odour was not perceptible beforehand.

From this circumstance we may conclude, that sulphurous acid has the property of combining, in small quantity, with animal substances, without experiencing decomposition ; in which state it can disguise some colours, particularly that arising from a combination of oxygen. But it would seem, that in the lapse of time a more intimate union is effected between the sulphurous gas and the oxygen.

This latter effect immediately takes place when sulphurous acid is made to counteract the chlorine. The yellowed silk is

\* Journ. de phys. 1774.

whitened by the sulphurous acid; and the two operations may be alternated. We shall have occasion to speak of the use which Giobert has made of this property.

We are obliged to confine ourselves to these conjectural views concerning the action which nitric acid, chlorine, and sulphurous acid, exercise on animal substances, till experience shall have conducted us to positive results.

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## CHAPTER V.

### *Recapitulation of the Theory laid down in this Section.*

SUBSTANCES which have constant colours should not be confounded with those which owe their variable and fugitive hues to the dimensions and density of the plates of which they are formed; or, at least, the theory of the one cannot serve for the explanation of the properties which the others possess, in reference to the colours which appear to depend on their peculiar affinity for the rays of light.

Meanwhile, till chemistry can be reconciled with physics, in explaining the phenomena exhibited by colours, we must content ourselves, in reference to the art of dyeing, with determining the affinities which characterize the colouring substances, and the physical dispositions which modify their action in every variety of circumstance.

Metallic colours must be distinguished from those which belong to vegetable and animal substances.

The colours of metals are modified and changed by oxydation, and in proportion to the quantity of oxygen combined with them.

The vegetable and animal substances, which occasionally owe to plates on their surface some plays of fugitive colours, may themselves have a peculiar colour, or may indeed owe their colours to coloured molecules which exist combined, or simply mixed with them. It is molecules of this kind, extracted from several substances, which receive different preparations, in order to serve for the purposes of dyeing.

The affinities of the colouring particles for acids, alkalies

earths, metallic oxydes, and wool, silk, cotton, and flax, constitute their chief distinctive properties; but these are modified by their physical qualities, and especially by their tendency to assume the solid, or to continue in the liquid state.

In consequence of the affinity between the colouring particles, and wool, silk, cotton, and flax, they combine more or less easily, more or less intimately, with each of these substances: from which arises a primary difference in the processes employed, according to the nature of the stuff and of the colouring substance.

Sometimes they unite immediately with the stuffs, but more frequently they require a mordant, in order to be separated from the solvent, and to be fixed on the stuff, or at least to acquire a greater permanence.

From the affinity of the colouring particles for alumina and metallic oxydes, they form compounds with these substances, in which their colour is more or less preserved, while it becomes more stable, and more insensible to external agents. This combination being formed of principles which possess the faculty of uniting to vegetable, and particularly to animal substances, has also itself this property; it enters into triple combinations with the stuff, and the colour resulting from this triple union thus acquires greater fixity, or the faculty of better resisting external agents.

The colouring particles have frequently such an affinity for alumina and the metallic oxydes, that they separate them from the acids which held them in solution, and fall down with these bases; but sometimes the affinity of the stuff must determine this combination. We have to distinguish between the chemical action of the substances which dissolve the colouring particles, and those which fix them, or effect their destruction.

Colours experience great changes from the action of oxygen, which eventually destroys them; the other substances promote or obstruct this action.

Of the two principles which compose the atmospheric air, it is only the oxygen gas which acts on the colouring particles. It combines with them, and thus impairs their colour or makes them pale. But its action is soon chiefly exerted on the hydrogen, which enters into their composition, and it thereby forms water. This effect may be compared to that of a feeble

combustion. Hence, the carbon which enters into the composition of the colouring particles becomes predominant, and the colour usually passes to yellow, dun, or brown; or this degradation, blended with what remains of the first colour, or with the effect at the same time suffered by a metallic oxyde, produces other appearances.

Light promotes this decomposition of the colouring particles, which frequently takes place only with its concurrence; and thus it contributes to the destruction of colours. Heat favours it also, but less efficaciously than light, unless it have a certain intensity.\*

The oxygen present in the colouring particles may itself undergo a combination productive of a slow alteration in the colouring particles, especially by the action of light and heat.

The oxygen which is absorbed does not, however, always and immediately produce that kind of combustion which alters and destroys the colouring particles; on the contrary, a certain absorption is usually necessary to give the colours lustre, or even to bring them out, while a larger proportion causes the colour to disappear; and it is but secondarily that the combination of hydrogen is formed, which produces the appearances of a slight combustion.

The colours are more or less durable, more or less fixed in the air, according to the greater or less tendency which the colouring particles have to experience that change, and to suffer it in a greater or less degree; for the resistance to this decomposition increases as it advances.

The other substances exercise their action on the colouring particles, either before they have been applied to the stuffs, or after they have been fixed on them; they thus have a different use, or they may produce destructive effects.

The substances capable of dissolving the colouring particles, serve to separate them from the particles with which they are confounded; and they prepare them, by the liquidity they communicate, for the action of the stuffs that are to fix them, or for the combinations they are to form.

The colouring particles are sometimes modified as to their colours by the action of these substances, and as they usually

\* *Statique chimique*, tom. i. p. 197.

retain a portion of them in the combinations which they afterwards form; or as, when the compound is formed, this may take a portion of them by sur-composition, we call these substances *alterants*, in order to contrast their effect with that of mordants.

We give the name of *mordants* to substances which, combining with the colouring matters, serve to precipitate, to fix, and to render them more durable.

These two genera of substances, therefore, which exercise the same chemical action, are distinguishable by this;—the alterants, in consequence of their physical qualities, attenuate and dissolve the colouring matters, so that only a small portion can remain in combination when the colouring substances assume the solid state; such are the acids and alkalies properly called, which, when they act with a certain energy, even deprive the stuffs of those colouring particles which were fixed on them. The power of resisting the action of them and of the air, constitutes the permanency of colours.

The substances, on the contrary, which naturally tend to the solid state, communicate this property to the colouring substances with which they have an affinity, serving as *intermedia* between them and the stuffs, with which also they must have a tendency to combine.

The mordants produce this effect only sometimes, and change but slightly the natural colour of a substance; alumina, in particular, has this property. Sometimes the colour of the combination results from that of the tinctorial substance, joined to that of the mordant; such are the metallic oxydes, which, moreover, alter or ameliorate the natural colour by the action of their oxygen. Thence arise their different effects.

1. The metallic oxydes, to which the oxygen adheres loosely, are not fit to serve as *intermedia* to the colouring particles, because they produce in them too considerable an oxydation. The oxydes of silver, gold, and mercury, are in this predicament.

2. The oxydes which, on giving up more or less of their oxygen, experience considerable changes in their colour, are also bad *intermedia*, especially for light shades, because they produce variable colours. Such are the oxydes of copper, lead, and bismuth.

3. The oxydes which retain their oxygen with force, and



which change their colour very little when they have lost a portion of it, are the most proper for accomplishing this object. The oxyde of tin must be here particularly distinguished. It easily abandons its solvent; it has a strong affinity for the colouring particles, and affords them a very white base, one capable of giving brilliancy to their hues, without altering them by the mixture of another colour. The oxyde of zinc possesses these properties in part.

In order to account for the colours that result from the combination of the colouring particles with the basis which a mordant gives them, we must also pay attention to the proportion in which the colouring particles are united with this basis. Thus, the solution of tin, which forms a very abundant precipitate with a solution of the colouring particles, proving thereby that the oxyde of tin enters in large proportion into the precipitate, influences the colour of the precipitate, by the colour of the base, much more than the solution of (sulphate of) zinc and of alum does, which bodies usually form a much less considerable precipitate. The precipitates produced by the two latter substances retain very nearly the natural colour of the colouring particles.

In the action of mordants, therefore, we must distinguish the combinations formed, by their means, between the colouring particles and the intermedium which they furnish to the stuff; the proportions of the colouring substance and the intermedium; the modifications of colour resulting from the association of the colour of the colouring particles with the base to which they are united; and finally, the changes which the colouring particles may suffer by the action exerted on them by that base.

Astringents do not differ essentially from colouring particles; but the latter take this name, especially when employed to produce black with oxyde of iron, by restoring this metal to the state of a black oxyde, and by their assuming a dark colour from the action of oxygen.

The notion of an astringent supposes, moreover, the property of combining in a certain quantity with animal substances, giving them thus solidity and incorruptibility; because these two properties are most commonly united. These again are derived from their large share of carbon, a circumstance in their com-

position which gives them increased tendency to solidity, and greater stability.

The natural properties of vegetable and animal substances must depend on those of their elements, and consequently on the proportions of these. These elements are principally oxygen, hydrogen, azote, and carbon. The first three, naturally very elastic, enter into solid combinations only by means of a force that subdues their elasticity. This again produces more or less effect, according to the temperature or the circumstances which may cause the repressing (condensing) force to vary. The carbon, on the other hand, must have a great disposition to assume the solid state, and to maintain its constitution.

## SECTION II.

OF THE DIFFERENCES WHICH DISTINGUISH WOOL, SILK, COTTON, AND LINEN (FLAX), AND OF THE OPERATIONS BY WHICH THESE SUBSTANCES ARE DISPOSED TO RECEIVE DYES.

### CHAPTER I.

#### *Considerations on the differences between Animal and Vegetable Substances.*

WE must not flatter ourselves that we can account for the different results of organization. The knowledge which we have acquired, however, of the composition of animal and vegetable substances, may, agreeably to the preceding considerations, give us some idea of the cause of the different tendencies which wool, silk, cotton, and flax have to unite with the colouring particles, and with the bases which constitute their mordants.

Wool and silk belong to animal substances; cotton, flax, and hemp, to vegetable.

The principal distinction between the composition of animal and vegetable substances is, that animal substances contain the peculiar principle, *azote*, in abundance, which, in the elastic state, forms what was formerly called phlogisticated air, or phlogisticated gas, and which exists in only a very small quantity in vegetable substances. 2. Animal substances contain much more hydrogen, or the basis of inflammable air.\*

\* Modern researches do not justify this position of M. Berthollet. Sugar and starch, by the analyses of MM. Gay Lussac and Berzelius, contain about as much hydrogen as fibrin does, and very little less than gelatin and albumen; while, by my analyses, wool and silk contain *less* hydrogen than cotton and flax.—See Phil. Trans. for 1822.

I subjoin the results of my analytical experiments on the four principal subjects of dyeing.

	Carbon.	Hydrogen.	Oxygen.	Azote.
Wool . .	53.70	2.80	31.20	12.30
Silk . .	50.69	3.94	34.04	11.33
Cotton . .	42.11	5.06	52.83	
Flax . .	42.81	5.50	51.70	

The first two, independently of the azote, possess a marked difference of composition, from their excess of carbon and deficiency of oxygen.—T.

From these two causes, the differences observed in the distillation of animal and vegetable substances arise. The former produce much ammonia, which is a compound of azote and hydrogen; the latter yield very little, and they afford usually even a good deal of acid, the characteristic properties of which flow from oxygen. From the former much oil is obtained, whose predominant principle being hydrogen, it has a great tendency to volatilize, and to separate at a slightly elevated temperature. The latter often afford no perceptible quantity of it. The former can produce prussic acid, which is a combination of azote, hydrogen, and carbon; and vegetables possess this property only in so far as they contain azote. In consequence of this composition, animal substances yield, on being burned, a lively flame, which bursts forth at the commencement; but this flame is, so to speak, speedily quenched by the charcoal that is evolved, which has peculiar characters. Their combustion is accompanied with a penetrating odour, arising from the ammonia and oil formed, which escape inflammation. They are subject to putrefaction, during which ammonia is produced, as it is in distillation, by the more intimate union of the azote and the hydrogen; whereas vegetable substances undergo a spirituous or acid fermentation. We merely indicate in this place ideas which have been developed in particular memoirs.

As animal substances contain a great deal of those principles which tend to assume the elastic state, they have less cohesion in their molecules than vegetables, and less stability in their composition. We may observe, that when they acquire solidity, they owe it most frequently to the mixture, or rather combination, of a foreign substance, such as the phosphate or carbonate of lime in the bones.

Hence, they are more subject to be destroyed by different agents, and more disposed to enter into combination with the colouring particles.

Thus, fixed alkalis, when pure or caustic, destroy animal substances, because they combine with them to saturation, and thereby lose their causticity.\*

From this action of alkalis on animal substances, it follows, that these substances cannot resist leys, and that alkalis must be had recourse to with much caution in the processes wherein

\* Mem. de l'academie, 1783.

such bodies are dyed; whereas the moderate use of alkalies is not to be dreaded with regard to vegetable substances.

Nitric and sulphuric acids have also considerable action on animal substances. The former decomposes them, with the disengagement of azote, the separation of fat or adipocere, and the formation of carbonic and oxalic acids from a portion of the hydrogen and the carbon. The latter acid disengages from them inflammable gas, and probably azotic gas, while it reduces the other principles into the carbonaceous state.

Silk appears to approach a little towards vegetable substances, from its inferior disposition to combine with the colouring particles, and from its greater resistance to the action of alkalies and acids. This may arise either from the same principles being here more intimately combined than they are in wool, or more probably from the presence in it of less azote and less hydrogen.\* But although the alkalies and the acids exert a less lively action on silk than on wool, we must nevertheless use them with much precaution, because the brilliancy of colour sought for in silk appears to depend on the polish of its surface, which we must beware of injuring.

Cotton resists the action of acids better than flax and hemp; and it is with difficulty destroyed even by the nitric acid.

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## CHAPTER II.

### *Of Wool.*

IN the cloth manufactures wool is destined to different purposes according to the length and fineness of its filaments; but there is a wide distance between the production of fine wooled sheep and ordinary wool. Hence no little gratitude is due to d'Aubenton for fixing public attention on this important object of agricultural economy, and to those individuals who have since prosecuted, with so much steadiness and success, the project of renovating our degenerate breeds by means of Merinos.

Wool is naturally coated with a species of fat, called grease.

\* The organic structure, and state of condensation in animal and vegetable fibres, should be studied along with their chemical composition, in order to learn their dyeing relations.—T.

This coating preserves it from the moths.\* Hence it is not scoured till it is going to be spun or dyed.

In order to scour wool, it is put for about a quarter of an hour into a boiler which contains a sufficient quantity of water, mingled with one fourth of putrefied urine. The whole is then heated as high as the hand can endure it, and it is stirred about from time to time with rods. It is now washed, and set to drain. The wool is removed thence into a large basket, placed in running water where it is stirred, till the grease having entirely left it, the water ceases to be milky. It is then taken to be drained. In this operation it loses sometimes more than a fourth of its weight. It is of great consequence that the scouring be carefully performed, because the wool is thus alone prepared for receiving the dye.

The residuum of the first operation is preserved in a tub, to which, from time to time, some putrefied urine is added, so that the grease present in it may serve to render more soluble any thing adhering to the new wool. The ammonia of the putrefied urine contributes probably to this effect. When wool resists this operation, a little soap is added to the liquor; but it is only with much precaution that the use of soap is permitted on fine wools, because it is apt to injure them.

Vauquelin† made experiments on the nature of the grease, from which it appears to be formed, 1, of a soap, with basis of potash, which forms its chief part; 2, of a small quantity of carbonate of potash; 3, of a notable quantity of acetate of potash; 4, of lime, whose state of combination he could not determine; 5, of a small quantity of muriate of potash; lastly, of an animal matter, to which he ascribes the peculiar odour of the grease.

He regards the ammonia contained in the putrefied urine as not being conducive to its action, and he even advises the use of ordinary soap as better fitted to procure the desired whiteness to wools; but experience leads to results incompatible with the opinion of this skilful chemist.

Wool is dyed in the fleece, or without being spun, principally when it is to be employed for forming cloths of mixed colours; or otherwise it is dyed after being spun. It is then intended chiefly for carpets, but it is most commonly dyed in the form of cloth.

\* Reaumur remarked, that it was sufficient to rub a stuff with greasy wool to preserve it from moths. — *Mem. de l'academie*, 1728.

† *Ann. de chimie*, tom. xlvii.

When wool is dyed in the fleece, its unconnected filaments absorb a greater quantity of the colouring particles than when it is spun; for a like reason, woollen yarn consumes more colour than woollen cloth. Cloths, however, exhibit much variety among them, according to their degree of fineness, and the closeness of their texture: besides, the difference of their dimensions, the variable qualities of the dyeing ingredients made use of, and the different circumstances of the operations, teach us not to confide in the precise doses enjoined in the processes usually described. This observation may be extended to all dyes.

For the generality of dyes, wool requires to be prepared with a bath, in which it is boiled along with saline substances, principally alum and tartar. This is called the *bouillon*, which we shall take care to describe under the different processes. But there are dyes for which wool needs none of these preparations. It must, however, be well softened in tepid water, and thereafter squeezed, or set to drain. This is a precaution which must in general be taken with all substances which we wish to dye, that the colour may more easily be introduced into them, and more equally distributed. Wool, in particular, requires heat to enable it to absorb the colouring particles; a circumstance which appears to depend on the disposition of its filaments to form a dense texture.

Monge has explained the mechanism of felting, and the effects of fulling, by the external conformation of wool, and the hairs of animals. He has made interesting observations on this subject, of which I shall relate the principal.\*

Nothing peculiar can be discovered on the outside of the fibres of wool and the hairs of animals by means of the microscope; yet "the surfaces of these objects are not smooth; they must be formed either of plates, which cover each other from the root to the point, nearly as the scales of fish overlap each other from the head of the animal towards its tail; or rather perhaps of superposed zones, as is observed in horns.

"If we seize a hair by the root with one hand, and draw it through the two fingers of the other, from the root towards the point, we experience scarcely any friction, or any resistance, nor do we perceive any noise; but if, on pinching it by the

\* Observations sur le mécanisme du feutrage.—Ann. de chimie, tom. vi.

point, we make it slide equally between the fingers of the other hand, from the point towards the root, we experience a resistance which does not exist in the first case, and a tremulousness perceptible to the touch is produced, which is also manifested by an audible sound.

“ We thus perceive that the contexture of the surface of the hair is not the same from the root towards the point, as from the point towards the root, and that a hair, when pressed, ought to experience more resistance in sliding and taking a progressive movement towards the point, than in sliding towards the root; but as this very contexture forms the principal object of this memoir, it is necessary still farther to confirm it by some other observations.

“ If, after seizing a hair between the thumb and the forefinger, we make the two fingers slide alternately one over the other in the direction of the length of the hair, the hair takes a progressive movement in the direction of its length, and this movement is always towards the root. This effect does not depend either on the nature of the skin of the fingers or on its contexture, for if we turn back the hair, so that its point is placed where its root was, the movement takes place reciprocally in the contrary direction; that is to say, it is turned always towards the root.

“ These observations, to which Monge adds some others, are all referred to the hair of his head taken as an example; but they equally hold true of horse hair, fibres of wool, and in general of the hairs of all animals. The surface of all these objects, therefore, is formed of rigid plates, superposed or tiled from the root to the point, permitting the progressive movement towards the root, and resisting a similar movement towards the point.

“ This conformation is the main cause of the tendency to felting, which the hairs of all animals in general possess.

“ The hatter, in fact, on striking with the cord of his bow the flocks of wool, detaches and disperses in the air each of the particular fibres; these fibres fall down over one another in all directions on the table, where they form a layer of a certain thickness. The workman then covers them up with a cloth, which he presses with his outstretched hands, working them about in different directions. The pressure approximates towards



each other the woollen fibres, and multiplies their points of contact; the agitation gives each of them a progressive movement towards the root. By means of this movement the hairs interlace, and the *lamellæ* of each hair, by hooking into those of other hairs which lie in an opposite direction, maintain the whole in the compact texture which the pressure first gave. In proportion as the tissue is compacted, the pressure of the hands ought to increase, both for the further condensation, and for promoting the progressive movement of the hairs, as well as their interlacement, which now meets with greater difficulty. But in all this operation the fibres of wool grapple only with one another, and not with the cloth, whose fibres, as we have already said, are smooth, and do not present the same facility in this respect.

“ The conformation at the surface, of the fibres of wool and the hairs of animals, does not constitute their sole disposition to felting. It is not enough that every fibre shall take a progressive movement towards the root; it is not enough that the inclined *lamellæ*, on grappling with one another, shall maintain the texture in the state into which the compression has put it; —it is further requisite, that the fibres shall not be straight like needles; in consequence of the agitation, each of them would continue its progressive movement without changing its direction, and the effect of the operation would be, to remove them all from the centre without producing any tissue. It is necessary, therefore, that each fibre should be twisted, that the extremity which is on the side next the root be disposed continually to change its direction, to interlace itself around new fibres, and to turn back on the fibre itself, if so determined by some change in the position of the rest of its length. Wool being naturally constructed in this manner, is peculiarly well adapted for felting, and may be so employed without being subjected to any previous operation.

“ But the furs of the rabbit, the hare, and the beaver, are naturally straight; they cannot be employed alone for felting, without having undergone a preliminary operation, which is called *secretage*; and which consists in rubbing them, before they are stripped off, with a brush moistened with a solution of mercury in nitric acid. This solution, by acting on only one side of the substance of the hairs, alters their right-lined

direction, and communicates the disposition for felting which wool naturally possesses.

“ The operation of *fulling* woollen stuffs, has so close a relation with felting, that we cannot dispense with entering into some details on this subject.

“ The roughness with which the fibres of wool are bristled at their surface, and the disposition which the fibres have to take a progressive movement in the direction of the root, is an obstacle to the spinning of wool and to the fabrication of stuffs. In order to spin the wool, and afterwards weave it, we are obliged to coat all the fibres with a film of oil, which, by filling up the cavities, renders the asperities less perceptible; just as a film of oil is put upon a smooth file, when we wish to render it still smoother. When the piece of stuff is manufactured, it must be deprived of this oil, which gives it a disagreeable colour, and constitutes a kind of filthiness, which would be an obstacle to dyeing. For this purpose, it is carried to the fulling-mill, where it is beat with mallets in a trough filled with water through which clay (fuller's earth) has been diffused. The clay combines with the oil, which it renders soluble in water; both are carried off by the fresh water which the machine itself brings upon it; and at the end of a certain time the stuff is scoured.

“ But scouring is not the only object of the fulling. The alternate compressions which the beetles exert on the piece of stuff, especially when the scouring is well advanced, produce an effect analogous to that of the hand-pressure of the hatter. The fibres of wool which compose one of the threads of the woof or of the warp, take a progressive movement, get introduced into one of the neighbouring threads, then into those which follow, and soon all the threads both of the woof and warp are felted together. The stuff, after having suffered a narrowing in its two dimensions, partakes of the nature both of web and felt; it may be cut without being liable to open out its threads, and there is no necessity for hemming the different pieces which enter into the composition of a garment. If it be ordinary knit wool, the stitch is no longer apt to run when it happens to escape. Lastly, the threads of the woof and the warp being no longer so well defined, or so distinct from each other, the stuff, which in other respects is thickened, forms a warmer clothing.”

## CHAPTER III.

*Of Silk.*

SILK is naturally coated with a substance, which has been regarded as a gum, to which it owes its stiffness and elasticity. The silk most common in our climates, contains besides a yellow colouring matter.

The greater part of the uses to which silk is destined, require it to be not only deprived of its colouring matter, but also of the gum. This twofold object is accomplished by means of soap. The name of *décreusage* (scouring) is given to the operation by which silk acquires its pliancy and whiteness.

The scouring must not be so complete for the silks which are to be dyed as for those intended to remain white; and it should even differ according to the colours proposed to be given. This difference chiefly consists in the proportion of soap that is employed. Thus, for ordinary colours, we content ourselves with boiling the silk for three or four hours in a solution containing 20 parts of soap for every 100 parts of silk, taking care to fill up the boiler from time to time with water, in order to have always a sufficiently large bath. The quantity of soap is increased for silks which are to be dyed blue, and more especially for those which are to be dyed *ponceau* (flesh-red), cherry colour, &c.; because these colours require a whiter ground than the less delicate ones. In treating of each colour, the proportions of soap suitable for the silk are indicated.

When silk is to be used white, it is made to undergo three operations. The first is called *dégommage* (ungumming). It consists in keeping its hanks in a solution of 30 parts of soap for 100 of silk. This solution must be very hot, but not in ebullition. When the dipped portion of the hanks is entirely ungummed, which is known by the silk assuming whiteness and flexibility, the hanks are turned about (shaken over) on the rods in order to subject the portion which had not been plunged to the same operation; and they are then withdrawn from the bath, and fastened on pegs, in proportion as the ungumming is finished.

The second operation is *the boil*. The silks are enclosed in

bags of coarse cloth, 26 to 33 pounds of silk being put in each bag, called a *poché* (pocket). A soap-bath similar to the former is prepared, with a smaller proportion of soap; and they are boiled for an hour and a half, taking care to stir about the bags, so that those which touch the bottom may not experience too great a heat.

The third operation is called *whitening*. This operation is intended principally to give the silk a slight shade, which may render the white more agreeable. Different names are given to the white, according to the shade. Thus we have china-white, silver-white, azure-white, thread-white. A solution of soap is made, such that, on beating it, a froth is obtained from which we may judge if it be of a proper strength. For the china-white, which should have a somewhat red cast, a little anotto is added. The silk is then left in it till it takes the desired shade. To the other whites more or less of a blue cast is given by means of azure, which is added to the solution of the soap, though some of it has already been put into the boil.

To prepare the azure, some fine indigo is washed two or three times in water moderately hot, when it is well ground in a mortar, and boiling water is thrown over it. It is allowed to settle, and the liquid is used, which retains only the most subtile parts. This is called *azure*; for which may be substituted a little of the liquor of a fresh vat of indigo.

At Lyons, where a more perfect white is given than at Paris, no soap is employed for the third operation; but after the second, the silks are washed, sulphured, and passed through azure diffused in river water. In this method, it is of importance to employ a very limpid water.—When the silks have become very uniform, and have taken the wished-for shade, they are wrung out and dried.

The white obtained by the method now pointed out, is not brilliant enough for silks intended for white stuffs. They must still be exposed to the fumes of sulphur. This operation will be described in the article on sulphur.

Since soap appears to injure the lustre of silk, the Academy of Lyons proposed, in 1761, as the subject of a prize, to find a method of scouring silks without soap; and this prize was adjudged to Rigaut de St. Quentin, who proposed to substitute for soap a solution of salt of soda, or carbonate of soda, dissolved in

a quantity of water large enough not to affect the silk. But inconveniences must have been found in the employment of this method, which was probably too active, since no use is made of it, although it is known, and may be easily practised.

Collomb\* published some observations on the bleaching of silk by the action of water alone, which merit much attention. Having perceived that a hank of yellow silk, which he had boiled about three hours in common water, had lost nearly an eighth of its weight, he repeated the ebullition twice, and carried by this means the diminution of weight to a fourth.

The silk which suffered this loss of weight, preserves, however, a yellow, or rather a chamois colour, which renders it unfit for making stuffs intended to remain white, or to receive some colours whose beauty depends on the whiteness of the ground to which they are applied; but it answers very well for colours which that tinge cannot injure. Thus the black dye which it took appeared preferable to that of silk bleached with soap.

After this operation, the silk remains very strong and tough, and threads of it supported weights which broke threads bleached with soap.

Eight hours of brisk ebullition are required for dissolving away the whole varnish of silk, in which it loses a little more than one fourth of its weight; but the ebullition ought to last longer when the barometer is low, because the greater the weight of the atmosphere, the higher is the degree of heat which boiling water takes.

This consideration led Collomb to try the boiling of silk in a Papin's digester; and in fact, it required only an hour and a quarter to effect the complete solution of the varnish, although the degree of heat was inferior to what produced some of the phenomena observed by philosophers in this concentrated ebullition.

The substance which the water dissolved, when evaporated, was black, brittle, and brilliant in its fracture. On distillation, it afforded the usual products of animal matter. It dissolved readily in hot water, leaving very little on the filter. The solution, which was clear, and of a greenish yellow colour, was not sensibly affected by acids or alkalis.

The solution of alum produced in it a precipitate of a dirty-

\* Observations sur la dissolution du vernis de la soie.—*Journ. de phys., Acad.*, 1785.

white colour; that of sulphate of copper, a black-brown precipitate; that of sulphate of iron, a brown precipitate; the nitromuriatic solution of tin, a white precipitate; the acetate of lead, a brown precipitate.

All these precipitates are scanty, and more or less viscid. Infusion of nut-galls, and of sumach, occasioned a white precipitate.

Alcohol does not dissolve this substance even by ebullition, but only a yellow colouring portion. This solution left, on evaporation, a scaly residuum of an amber-yellow. On boiling 15 grains of this substance in 1500 grains of alcohol, containing some drops of muriatic acid, its solution was effected, but, on cooling, this substance took the form of jelly.

The substance taken from silk in the scouring, is therefore of an animal nature; whence the soap-water which has served for the scouring speedily putrefies. When this substance is no longer retained by its affinity for silk, it becomes soluble in water, but not in alcohol. Although it is not of a vegetable nature, the term *gum* seems sufficiently proper. The yellow colouring matter dissolves in alcohol. When this part is separated, the gum becomes brown. It would seem that this colour is caused by the heat of ebullition, since, when the yellow colouring portion only is removed by the process of Baumé, of which we shall presently speak, the silk remains white.

In the process of Collomb, the gum is removed, carrying with it only a portion of the yellow colouring particles; while, in scouring with soap, the gum, and yellow colouring parts, are both carried off from the silk.

When silk is intended for the manufacture of blonds, laces, and gauzes, it should have its natural stiffness and elasticity. The greater part of the silk produced in our climates has a yellow colour. The white silk of China is therefore principally employed for these objects, and a few others. It is not yet positively ascertained whether the Chinese silk is naturally white, or rendered so by some unknown process. According to Poivre, this silk is bleached by exposing it to the sun. But some other circumstance is necessary; for this method has been tried without success. Baumé has published a process which he considers as analogous to the Chinese one.\*

\* Ann. de chimie, tom. xvii.

This process consists, 1. In infusing the yellow silk, or that which has not naturally a sufficiently pure white, in water heated to 88° Fahr., to destroy the mutual adherence which the threads had contracted in the winding; 2. In making this silk undergo two successive macerations, longer or shorter according to the temperature, in a mixture of alcohol containing 1-64th of its weight of muriatic acid; 3. In washing the silk with much care immediately after this operation, which, on losing its colouring part, has given up but a portion of its gum; 4. In drying this silk in a state of extension, to prevent it from crisping. The muriatic acid employed ought to be thoroughly free from nitric acid, which gives, as we have seen, a yellow colour to animal substances. For the same reason, such muriatic acid must be avoided as has been rendered yellow by chlorine. Hermstadt affirms, that he repeated this operation with success.

A skilful chemist, Giobert, makes objections to this process, for which he substitutes a new one. We shall remark, meanwhile, that in his experiments he employed 1-48th of muriatic acid, while Baumé prescribed only 1-64th. We shall here present the extract which has been given of his work.\*

“The preparation of the acid pointed out by Baumé is very embarrassing. The green colour which the liquid assumes, the species of jelly which it forms around each filament, and still more the diminution of weight in the silk, are sufficient to indicate that it would not be correct to view in the action of this liquid only the destruction of the colouring matter. Even in retaining a portion of its rawness (*crud*), the silk is far from preserving so much of it as is desired in the arts; and this process, which involves considerable expense, becomes more costly than is imagined, from the diminution in the weight of the silk.

“Crell and Brugnatelli proposed chlorine. But it is known that silk comports itself in the same way with this acid as animal substances do, that is to say, it becomes yellow. Yet we shall presently see that it may be employed. When this substance is used in the form of gas, Giobert found that the silk was soon destroyed by it.

\* Bibliot. ital. tom. i.

“On employing it in the state of a pretty concentrated solution, the yellow colour becomes weaker, and apparently approaches to white; but on taking it out of the aqueous chlorine, the silk is of a yellowish colour, and this hue is more durable than its natural one.

“From this result it appears that chlorine exercises on silk a twofold action; that is to say, it destroys its colouring matter on the one hand, and on the other, it makes the same impression as on animal substances in general—a change indicated by a yellow tinge.

“This last impression is destroyed by the action of sulphurous acid; and it is in the combined and alternating action of it and chlorine that the author has attempted a new mode of bleaching.

“In the preceding experiments, and in all those where aqueous chlorine, however little concentrated, was employed, Giobert observed that the silk was considerably weakened. Very frequently, after being well washed, the filaments broke in the wringing.

“The same liquor diluted to a great degree no longer produced this effect, yet it exerted a well marked action on the colouring matter of the silk. On coming out of it, the silk retains a portion of its natural colour, and being a little oxygenated by the agency of the chlorine, it exhibits its effects and appearances.

“On passing it then into liquid sulphurous acid, also very dilute, the yellow tint is destroyed.

“Giobert has succeeded in whitening the silk completely and preserving its raw feel, by passing it alternately through these two liquids for ten or twelve times, finishing the operation with the sulphurous acid.

“It is of the greatest importance to multiply the immersions, and not to employ strong gaseous impregnations, by which the silk would be either destroyed or considerably weakened.

“Silk bleached by this method is scarcely diminished in weight. It retains its raw feel, its flexibility, and does not appear to get stiff, while the bleaching is uniform in all its parts.

“When it was compared with the silk bleached by the process of Baumé, the latter was found to present a more agreeable



gloss, while the former had merely a dead-white. This circumstance does not appear to Giobert very important, because the chief use of bleached raw silk is in the manufacture of gauzes; and much gloss is not required in this kind of stuffs.

“The dyers believe that silk which has received the fumes of sulphur is not well adapted to receive colours. Giobert attempted to rectify this principle with raw silk bleached by the process just detailed. This silk took every colour, and particularly the finest black.”

Aluming ought to be considered as one of the general operations of silk dyeing, because without alum the most part of colours applied to silk would possess neither beauty nor permanence.

To execute the aluming there is put into a tun or tub from 140 to 175 gallons of water, and 44 to 55 pounds of Roman alum, previously dissolved in a kettle-full of sufficiently hot water, stirring carefully during the mixture, to prevent the crystallization of the alum.

After washing and beetling the silks, and even wringing them on the jack and pin,\* to extract the soap which they may have retained, they are plunged into the alum bath. Here they are left for eight or nine hours, after which they are twisted by hand over the tun (vat), and taken to the river to be washed.

We may pass as much as 165 pounds of silk through a bath like the preceding, without being under the necessity of adding fresh alum. But when it is perceived that the bath begins to become weak, which habit teaches by the taste, 22 to 26 pounds of alum are dissolved, which are put into the bath, as at first; and thus it is continually renewed, till it begins to emit a disagreeable smell. It is then thoroughly exhausted by passing the silks through it which are intended for dull colours, such as browns, chesnuts; after which it is emptied out, and a new alum liquor formed.

Silks are always alumed in the cold, because, when they are alumed in a hot bath, they are apt to lose a portion of their lustre.

\* The usual frame for wringing hanks of yarn, with the aid of a screwed rod.—T.

## CHAPTER IV.

*Of Cotton.*

COTTON is the down or wool (*bourre*) contained in the pod of a plant which grows in hot countries. This down is separated from the seeds which it envelopes by means of a kind of mill.

Climate has a great influence on the qualities of cotton, and the species of the cotton plant seem to correspond to the degree of heat.\* But a great variety are found in the West India islands; and it appears from what Bennet says,† that the colonists have hitherto neglected to make a selection of those which would be most advantageous, whence they have lost a great part of the benefits which they might have derived from this valuable production.

Five species of the cotton shrub have been distinguished, which contain many varieties. Linnæus has distinguished these five species by the following names: *gossypeum arboreum*, or the cotton tree of India; *gossypeum religiosum*, a great shrub which grows also in India; *gossypeum Barbadense*, a biennial shrub cultivated in Barbadoes; *gossypeum hirsutum*, a shrub which is perennial in the hot climates of America, and annual in the cold; *gossypeum herbaceum*, which seems to be originally from Persia, but which is cultivated in the islands of the Archipelago, in Egypt, Malta, and Sicily. The Russians cultivate it even in the government of Caucasus.

To these species may be added the cotton of Siam, remarkable for the fineness and silkiness of its filaments.

According to Guthrie, there has been cultivated for some time in Germany an *asclepias*, *asclepias syriaca*, Linn. which yields a very silky species of cotton.‡ Manufactures have been established in Saxony of stuffs with this cotton, which rival silk in lustre.

\* Essais sur les caractères qui distinguent les cotons des diverses parties du monde, &c. par M. Quatremere Disjonval.

† Transactions of the Society instituted at London for the Encouragement of Arts, Manufactures, and Commerce, vol. i.

‡ Memoirs of Manchester, vol. v. part 1.

The principal differences of cotton consist in the length of its filaments, their fineness, their solidity, and their colour. In the last point of view, several species are distinguished in commerce, which differ not only in their absolute value, but also in the uses for which they are intended.

The colour of cotton varies from deep yellow to white. The highest coloured is that of Siam and Bengal; with which stuffs are often made that preserve the native hue.

Cotton has become, by the extent and variety of its uses, one of the principal objects of manufactures and commerce. From its manufacture being conducted with little expense of labour, India has particularly derived much of the treasure constantly poured into it.

A nation celebrated for its genius in the arts, has succeeded in compensating the difference in the rate of wages by the expedition of machinery, and has thus drawn into its bosom this source of prosperity. It must preserve exclusively the great advantages which it now derives, were other nations not to endeavour to promote, by particular measures of administration, a competition of manufacture capable of supporting a part of their population.\*

To prepare cotton to receive the dye, it is subjected to an operation, called in French *décreusage* (scouring.) Some persons boil it in sour water; but most frequently an alkaline ley is employed. In this the cotton is boiled for two hours, after

\* Some respectable philosophers, while claiming freedom for commerce and industry, appear to have made too wide an application of their principles of political economy, when they inveigh against those restraints which the vigilance of government puts on the introduction of particular products of foreign manufacture.

When manufactures have acquired a marked superiority by peculiar processes, when long practice has carried these processes to perfection, and when the dexterity acquired by their workmen bids defiance to competition, we must for ever renounce them, or these advantages must be balanced by import duties, or even by prohibitions.

It is said, that we thereby force capital into other directions less natural and advantageous. This maxim is true with regard to objects in which manufactures possess natural advantages or disadvantages.

But when merely temporary disadvantages are to be counterbalanced, when an object of great consumption is concerned, which may afford employment to a large portion of the population, it is the interest of the consumers themselves to submit to a temporary impost, which may serve as a premium to a new branch of industry, and may even create sufficient capitals to those who undertake it, by affording extraordinary profits up to a certain stage. They are in the predicament of a landed proprietor, who renounces, for some time, a part of his revenue, to establish a canal of irrigation on his estate.

which it is wrung out. It is then rinsed in the river till the water runs off clear, when it is dried.

Cotton cloth intended for printing is immersed for some time in water charged with one-fiftieth at most of sulphuric acid, after which it is washed with care in running water, and dried. The acid used in this operation dissolves the calcareous earth, and the oxyde of iron, which might have injured the colours.

The aluming is given in the proportion of a quarter of alum for one part of cotton. The alum is dissolved with the precautions pointed out in the preceding article, but a solution of soda is added to it, which may be estimated at about one part of soda for sixteen of alum. Some persons introduce a very small quantity of tartar and arsenic. The yarn is well impregnated with this solution, by working it in small portions; after which the remainder of the bath is poured upon the whole yarn collected in a vessel. It is left there for twenty-four hours. On coming out of the aluming, it is set to purge itself in running water for an hour and a half or two hours, and it is then washed. Cotton absorbs about one-fortieth of its weight in this operation.

The galling is made with different proportions of gall-nuts or other astringents, according to the quality of the astringent, and the effect wished to be obtained.

The gall-nuts, bruised, are to be boiled about two hours in a quantity of water, which ought to be proportioned to the quantity of yarn to be galled. The bath is then allowed to cool, so that the hand may bear dipping in it. It is divided into portions, which are made as equal as possible, in order to operate with small parcels, as is mentioned under aluming; and the remaining liquor is in like manner thrown over the whole. Here it is left for twenty-four hours, especially when it is intended for maddering and for black; with regard to other colours, from twelve to fifteen hours may suffice; after which it is wrung out and dried.

When the galling is given to stuffs that have already received a colour, it must be done in the cold, in order not to alter this colour.

Alumed cotton takes a greater increase of weight in the galling than what is not alumed; for although alumina fixes in only small quantity on cotton, it communicates to it the property of combining much better with the astringent principle, as also with the colouring particles.

## CHAPTER V.

*Of Flax and Hemp.*

SINCE flax and hemp present the same properties, in reference to dyeing, they are usually confounded together in this work.

If cotton be an important object to our industry, flax and hemp merit peculiar attention, both as a territorial production, and as the most extensive source of employment to the people. This manufacture is spread over the whole country, and is subdivided into branches, from the fabrication of cordage to that of lace, and it fills up the intervals of rural labours.

One consideration which ought not to be overlooked, is, that the land most proper for hemp is that of marshes, from which the water has been drained, and that it is a production particularly adapted to small cultivators.\*

Flax and hemp must undergo several preparations before they can receive a dye. The first is steeping, by which the bark of the plant is rendered separable, so as to become fit for spinning. Steeping is an operation of such importance, from the influence which it possesses on the quality and quantity of the product, and from the deleterious qualities which it may communicate to the air, that it is proper to give some idea of the principles on which it should be conducted. The steeping of flax, in particular, has engaged the attention of practical men.

In steeping, it appears that a glutinous juice, which holds the green colouring part of the plant in solution, and which unites its cortical with its ligneous portion, suffers a more or less complete putrefaction, according to the method employed; for, as Rozier remarked,† carbonic acid gas and inflammable gas are disengaged. This substance seems to resemble closely the glutinous portion dissolved in the juice expressed from green plants, which is separated along with the colouring particles

\* Instruction familière sur la culture et le roui du chanvre, à l'usage des gens de la campagne, par Pertuis.

† Essai sur la culture et le rouissage du chanvre, par l'Abbe Rozier.

when it is exposed to a heat bordering on ebullition, and which putrefies, and yields ammonia by distillation.

Although this substance be held in solution in the expressed juice of plants, there is a probability that water alone cannot separate it sufficiently from the cortical part; and hemp which has been steeped in too rapid a stream, wants pliancy and softness.

If the steeping be performed in stagnant waters, the hemp contracts a brown colour; but, above all, it loses its durability, and exhales vapours productive of dangerous maladies. What is steeped by exposing it merely to the action of the elements on the ground, is also weakened, and requires much time and manual labour.

It appears, therefore, that steeping is performed in the most advantageous manner in tanks placed on the banks of rivers, in which the water may be renewed, so much as to prevent a putrefaction hurtful to the hemp and detrimental to health, without obstructing the putrefaction necessary to render the glutinous substance soluble in water.

Rozier found, that the steeping process went on when the hemp was covered with a layer of earth, and he recommends this method; but it has been ascertained that the hemp was too easily affected in this operation.

Proset\* has proposed to mix a small quantity of caustic alkali with the water in which the steeping takes place, in order to increase its solvent power, and to prevent the putrefaction; but it appears from the experiments of Home, that alkalies retard the operation of the steeping, and render the flax liable to break.†

During the maceration, as well as the previous and subsequent drying, the green colouring particles suffer an alteration, like that observed in the green substance of plants which have been exposed to the action of air and the influence of light. Their colour passes to yellow, dun, or even brown, by an agency which we have compared to that of a slight combustion.

That substance is partly reduced into powder, which is dispersed during the dressing, rendering this operation dangerous to those who practise it. Another portion remains attached to

\* Mem. sur le rouissage du chanvre.

† Essay on Bleaching.

the fibres; but perhaps dissolved in the alkaline leys employed before the bleaching, whereby all this foreign matter ought to be separated.

For avoiding the acrid dust which rises during the hatcheling, Marcandier has recommended to macerate the fibres in small portions in hot water, to wash them with much care, and thereafter to dry them. By this means we may diminish the colouring matter, and render the flax or hemp softer and better prepared for the action of the hackle. He has even suggested the use of an alkaline solution.\*

On a more complete solution of the colouring particles, is founded a process published by the Prince de Saint-Sever, to obtain fine dressed hemp.† He recommends to put the tress of hemp in a ley made with a solution of two parts of soda to one of lime, next to impregnate it with soap, to digest it for some time, then to wash it well, and lastly, to hackle it. Several processes analogous to the preceding have since then been practised, under the veil of mystery. Their results had an imposing aspect. But experience has sufficiently shown, that besides the expense which they incurred, these processes increased the proportion of tow, and the yarn obtained had less durability, and little advantage in beauty over the yarn yielded by the unprepared hemp.

Bralle, an old curate of the department of the Somme, occupied himself regularly for several years with the means of improving the preparation of hemp, as an object of great national interest. His first attempts consisted in steeping hemp, as soon as it was taken from the ground. On coming out of the steeping, he separated the bark from it, which easily came off. After cutting the stem near the root, and dipping it in a weak solution of black soap, he washed it with much care before desiccation. The colouring portion which would have become insoluble, except in alkalies, may also be dissolved and carried off by water, assisted by a little soap. The fibre is then much whiter. By combining the action of the sun with this process, he succeeded in making it still whiter.

These operations had the inconvenience of requiring long

\* *Traité de chanvre.*

† *Journ. de physique, introd. tom. ii.*

and minute manipulations. Bralle, however, hit upon a process, by which a large quantity of hemp may be steeped in a few hours, with the advantage of freeing the stems from their bark without any waste, of preserving the length of the fibres, and consequently of producing much less tow.

The process of Bralle, whose efficacy has been verified at the *Conservatoire des Arts* on hemp intended for cordage and sail-cloth, has just been published by order of government. It consists in keeping the hemp plunged for two hours in water, containing a forty-eighth part of green soap (soft soap) in solution, which is maintained at a temperature of from 194° to 200° Fahr. (NOTE K.)

A mode has been discovered of giving to the dressed hemp, and even to the tow, a division and fineness which qualify it for the same spinning processes as cotton; so that with this preparation alone, or mixed with cotton, stuffs may be made which have a much more considerable value, than those of hemp in its natural state.

Marcandier seems to be the first who engaged in this process. He recommends to give to the tow, first of all, the preparation which he prescribed for the dressed hemp. "In carding it like wool, a fine medullary white substance is got, for which heretofore no use was known. It can be employed by itself in this state, not only to make ouates (fine cotton,) which, in many respects, is better than the ordinary ouates, but it may also be spun into a very fine yarn. It may likewise be mixed with cotton, silk, wool, and even hair; and the yarn resulting from these different mixtures, furnishes, in its numberless variety, materials for new trials interesting to the arts, and to several manufactures."

This object has engaged much attention in Germany. Hermstadt quotes several works which treat of it.\* He states, that, according to Meidinger, the staple of hemp acquires the elasticity of cotton, when, after being purified by a solution of pot-ash and muriate of soda, it is fixed on cylinders of wood, and dried in a stove. It is also asserted, says Hermstadt, that hemp takes a fine texture when its moist fibres are put into a wooden chest, with alternate layers of wood-ashes, closing the

\* *Grundris der Farbekunst.*



chest with a cover, and putting it into a stove, heated not just so high as to burn the wood.

Hermstadt informs us, that the hempen webs which have received these preparations, lose the appearance of cotton by repeated washings.

In treating of bleaching with chlorine, another process will be pointed out.

Flax and hemp intended to be dyed, must be subjected to the same operations as cotton, namely, scouring, aluming, and galling.

## SECTION III.

### ON BLEACHING BY THE OXYGENATED MURIATIC ACID, (CHLORINE.)

#### INTRODUCTION.

THE art of bleaching by chlorine, is a direct application of the chemical properties of this acid; for the first knowledge of which we are indebted to Scheele, but which were developed and submitted to a regular theory in 1785.

At this period, the first attempts at applying this acid (now the element chlorine) to bleaching were promulgated. These were soon prosecuted in England by the celebrated Watt, and afterwards by Bonjour, Descroizille, Welter, Widmer, and Haussmann. A description of this art, still in its infancy, was published in the *Annales de chimie* for 1789; meanwhile it continued to make some advances, which were successively published. A second description was given of it, chiefly on the data of Welter,\* who had persevered in its practice on the great scale; and those who are acquainted with this able chemist, know what confidence may be reposed in his observations.

Since then, different treatises on this process have appeared. We shall here give an idea of such of them as have come to our knowledge.

Pajot des Charmes published one,† which appeared in the year 8, (1799.) In this, he speaks only of the first description which had been given in the *Annales*, and neglects one which had been made public five years before his own work, and of which several separate editions had been given.

He represents the process which had been promulgated as very difficult to execute; but the corrections which he pretended to introduce, do not appear to us to have any other

\* *Journal des arts et manufactures.* An. 3.

† *L'art du blanchiment des toiles, fils, et coton de tout genre.*

effect than to diminish its precision or advantages. Thus he suppresses the intermediate vessel, which we considered to be useful. He recommends, as a very beneficial change, to substitute leaden tubes for those of glass. He mixes potash with the liquor (aqueous chlorine) to suppress its odour, the effect of which mixture had been appreciated in the original description; he regards the odour of chlorine, in the way it had been prescribed, as an insurmountable obstacle; and he gives an account of the distress which he had suffered in repeating this process. He would have become satisfied that the process might be executed without inconvenience, had he carefully followed the directions, or had he visited the establishments conducted by Widmer, Welter, or several others who used it at that period. He exclaims against the length to which the prescribed number of leys and immersions must give rise. *The limits of this number* had been said to be *between four and eight*, and we find (page 106 of his treatise) that he increases the leys to six, and the immersions to seven. He gives, moreover, a process for making sulphuric acid, by which sulphurous acid only can be obtained, &c.

Chaptal published a notice about a process long used for bleaching cotton in the southern parts of France,\* which had been pointed out in our second account of bleaching. The cotton is impregnated with a solution of soda, and subjected to the vapour of boiling water in a close vessel, where this vapour suffers compression; after which it is exposed for some days on the grass. This process gave occasion to O'Reilly to publish a work on bleaching.† We shall not discuss the method which he there extols, because his assertions have not hitherto been confirmed by the experiments to which they led several operators. We shall merely remark, that in the same work he describes an apparatus as well adapted to the preparation of chlorine; but this apparatus is such, that the vapour of the chlorine, by its elastic action, would cause all the water of the intermediate vessel to spout out by the tube of safety, which in fact would soon be emptied by the same cause. Several of his details show that he described from imagination.

\* Bulletin de la Société Philomatique. Brumaire, An. 8.

† Essai sur le blanchiment.

We owe to Westrumb\* a work on the new mode of bleaching; but this skilful chemist intimates, that he describes this art only from his own trials, without taking into account what experience had taught to actual practitioners. Rupp has given interesting experiments on this subject, of some of which we shall avail ourselves.†

We do not hope always to make the best selection in the operations which we are about to describe; but we shall be guided particularly by the observations of Widmer and Welter, who have conducted this process for several years with increasing success. We shall not advance, on views simply conjectural, even the modifications which might be contrived; but experience will undoubtedly teach us more and more to simplify, improve, and extend the usefulness of the process. Those who wish to employ it only on inconsiderable objects, by neglecting trifling interests, or by resting satisfied with partial effects, may easily simplify both the apparatus and the manipulations.

In particular cases, bleaching may be greatly abridged, and even reduced to a few hours; but we must study, in a manufacture, to establish a series of operations, the success of which shall be proof against accidents, and which shall steadily procure employment to the same workmen, rather than accelerate any particular process.

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## CHAPTER I.

### *Theory of Bleaching.*

CHEMISTRY has made such progress in our times, as to render an acquaintance with it indispensable to the practice of several arts; but the one which has for its object the bleaching of yarn and cloth by chlorine, requires, in particular, an operator to whom the science is not unknown.

Chlorine is the agent substituted in this mode of bleaching for atmospherical air, which requires tedious exposure on the grass. For directing its preparation and effects, we must therefore be well skilled in its properties.

Muriatic acid (the marine acid of the old chemists, and the

\* Bemerkungen und Vorschläge für Bleicher.

† Mem. of Manchester, vol. v.

hydrochloric of the modern French school) combines with oxygen, and thereby assumes the properties of chlorine; but to make this combination effective, the oxygen must have lost its elastic state. Thus it exists in the oxyde of manganese (manganese of commerce) in very considerable quantity. When, therefore, one part of oxyde of manganese is mixed with four parts of the fuming, or six parts of ordinary muriatic acid, one portion of the acid combines with the oxyde of manganese, with the disengagement of the oxygen superfluous to this combination, which combining immediately with another portion of the muriatic acid, thus forms the chlorine. The operation is promoted and completed by the action of heat. The chlorine assumes on its separation the gaseous state, when it is soluble in water. The resulting liquid is of a greenish-yellow colour, and of a very penetrating odour. If the temperature approaches that of freezing water, the chlorine gas becomes concrete, and adheres to the tube which conducts it into the water, whence it precipitates, so that the liquid is less impregnated than at a somewhat higher temperature.

It is easy to show that the oxyde of manganese contains much oxygen; for on urging it with a strong fire, it evolves a great quantity; after which the oxyde can produce but very little chlorine.

We may be easily satisfied also of the existence of oxygen in the chlorine. We have only to expose to the light of the sun a phial filled with the above liquid, from which phial a bent tube dips under a receiver filled with water. Bubbles of air are soon disengaged, which pass into the receiver, constituting an elastic fluid, which possesses all the properties of pure air or oxygen gas. When these bubbles cease to issue, the liquid has lost its odour, colour, and all its distinctive properties. It is now water impregnated with ordinary muriatic acid. The composition and decomposition therefore equally prove, that chlorine is simply a combination of muriatic acid and oxygen. But this speedy decomposition by light shows, that the oxygen very readily abandons the muriatic acid, either to assume the elastic state, or to enter into other combinations; and it is on this that the characteristic properties of chlorine depend.\*

\* See Note to page 38.

If vegetable colours be plunged into chlorine, they disappear more or less quickly; and when there is a mixture of different colouring particles, some disappear more readily than others, the whole, however, being more or less affected. When the chlorine has thus exhausted its action, it is found to be reduced to the state of ordinary muriatic acid; the colouring particles have therefore abstracted its oxygen. If we evaporate the liquid in order to examine the state of the colouring particles, we find that it yields a blackish residuum, as if its particles had suffered a slight combustion. (NOTE L.)

It is in this way also that colours are more or less speedily destroyed by the action of the air, especially when it is promoted by the solar beams, as was shown in the preceding section. Hence chlorine easily and quickly produces the effects which air and light operate in a longer space of time, because the oxygen, deprived in part of its elasticity, and adhering loosely to the acid, enters readily into combination with the substances for which it has an affinity.

The filaments of flax and hemp are enveloped in colouring particles, retained in them by a true combination, and which mask their whiteness. When these colouring particles combine with oxygen they are decomposed, so as to become soluble in alkalies. Hence the potash of the ley dissolves, and separates them from the filaments. On repeating several times the exposure on the grass, or the immersion in chlorine, and the action of the leys, we separate all the colouring particles of the filaments which remain white. By these operations the yarn loses nearly one-third of its weight.

If an acid be poured on the solution of the colouring particles in potash, and if we dry the precipitate formed, which remains upon a filter, it is blackish, and has the appearance of a body which has suffered a slight combustion, or has been carbonized. The ley, when saturated with the colouring particles, loses all its activity. What is here said of potash, is equally applicable to soda.

Yarn bleached by the ordinary process, or by that just described, has lost a portion of its strength, whence it no longer can sustain the same weight as before bleaching; but if both operations be made with equal care, the yarn bleached by means of chlorine preserves more strength than that which has been

treated by long exposure on the grass, because the leys have been less numerous, and the operations not nearly so long.

This mode of bleaching, then, is produced by the successive action of leys and of chlorine. We must therefore describe the apparatus and operations which the chlorine solution and the leys require, as well as the means of promoting their action, preventing their inconveniences, improving the whiteness, or giving to bleached objects the qualities that are desired. Lastly, we shall examine some other applications of the properties of chlorine.

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## CHAPTER II.

### *Of the Preparation of the Oxygenated Liquor, (Solution of Chlorine.)*

THE purpose of the apparatus used in this preparation is, to disengage the chlorine, and to combine it with water. It is therefore divided into two parts,—the one which comprehends the extrication of the gas, and the other its combination with water.

For the first object, a furnace is employed, capable of containing an iron pot to serve as a sand-bath. It is usually constructed of brick. The inspection of the plate will give an idea of one of these furnaces. In the sand bath is placed a matrass containing the mixture, to be subsequently described.

Matrasses from 15 to 17 inches in diameter are preferable to those of greater dimensions, because they are less liable to break, are more easily managed, and much cheaper. The elliptical form is more advantageous than the spherical, because with an equal diameter the capacity is greater. If one matrass be inadequate for procuring the liquor which is wanted, two furnaces can be placed alongside of each other, (See fig. 1, 3, 4.) which can be put in action successively, or at the same time.

The second part of the apparatus in which the gas is received, is the *receiver*. It has an interior diameter of nearly three feet, but it may be  $6\frac{1}{2}$  feet and even more in diameter. Its sides and its bottom ought to be formed of strong oaken staves, hooped with iron, and covered with a cement.

To protect the inside of the receiver, as well as the cisterns, from the action of the liquor, they must be covered with a

resinous coat, of a consistence not soft enough to run, or hard enough to break off in scales.

The interior of the receiver is furnished with three inverted tubs, (fig. 2. L L L) destined to receive the gas extricated from the matrass. The depth of each tub ought to be about 3 inches. Their connexion with one another does not admit of iron, which would be attacked by the chlorine. They are secured by transverse bars fixed to the circumference of the receiver. The space between the tubs and the sides of the receiver is closed, with the exception of an opening, which permits the liquor to communicate from one tub to another, and which ought to be placed alternately on the opposite sides, as may be seen, (fig. 1, 2.)

The inferior tub, as well as the middle one, carries in its bottom a glass tube, destined to transmit into the upper the chlorine, when the former are filled with it. This tube is half an inch shorter than the interior edge of the tub, (fig. 2. P P.)

Between the matrass and the receiver is a bottle, into which a little water is put. It has three tubulures. To one is adapted the tube of communication between the matrass and itself; from the second proceeds the conducting tube (K. fig. 2.) destined to convey the gas under the lowest tub of the receiver; the third receives a tube open at both ends, which bears the name of *tube of safety*, because it obviates absorption. To accomplish this object, it must have, reckoning from the level of the water in the bottle, a greater height than that of the portion of the conductor tube, which plunges into the liquor of the receiver; otherwise the water of the bottle, pressed upon by the gas, would escape at its upper part. The portion of this tube which dips into the water of the bottle should also be shorter than that of the conductor tube, which is above the level of the water of the receiver; so that when the vessels become cool, and a partial vacuum is formed, the external air may enter by the tube of safety before the water of the receiver can rush in through the conductor tube.

All the tubulures are shut with accuracy, but in different ways. The *tube of safety*, and the *conductor tube* are permanently fixed. With this view, they are passed across a hollow cork, which is coated inside and outside, with a mixture of wax and turpentine, and forcibly pressed into the tubulure.

The tube of *communication* between the matrass and the



intermediate bottle should have a stopper at each extremity; but as the stoppers must be removed at the end of each operation, they are not strongly pressed in, but merely covered with a bladder, coated with the same mixture, to protect them from the action of the gas; and they are fixed down by packthread, or rather by levers loaded with a weight at one of their ends.

Between the furnace and the intermediate bottle a deal partition is made, having an opening cut in it for the passage of the tube of communication.

It is useful to attach to the upper tub a pipe, having a bent extremity dipping into a vessel filled with solution of potash. When, by any circumstance, the gas comes to fill the cavity of this tub, the excess escapes by this pipe, and is absorbed by the potash, thus protecting the manufactory from the inconvenience which would result from its diffusion.

We may employ muriatic acid and oxyde of manganese directly, or we may substitute for the muriatic acid, sulphuric acid and muriate of soda, which salt, when decomposed by this acid, gives out the muriatic. The choice depends on the price of those substances at the establishment. The process which we are going to describe is the second one. It is the best, on the whole.

Oxyde of manganese (manganese of commerce,) when of good quality, is in black masses of greater or less size, composed of small needles of a metallic lustre. It should contain very little foreign mineral. It is reduced into powder, and well mixed with the salt, in the proportions to be presently stated.

If a manufacture of sulphuric acid be at hand, we may dispense with purchasing it concentrated, as it may be employed in the state in which it comes out of the leaden chamber, provided it have a proper degree of concentration.

Concentrated sulphuric acid, such as is found in commerce under the name of *oil of vitriol*, marks 168° by the hydrometer of Twaddell, (1.848 specific gravity.) It is here presumed to be in that state.

The proportions of the ingredients which appear to us most suitable are, 10 parts of oxyde of manganese, 20 parts of sulphuric acid concentrated to the above degree, and 27 parts of muriate of soda. We do not, however, affirm, that these are the most exact proportions which can be determined. (NOTE M.)

If the manganese is of inferior quality, which is discovered by the residuum of the operation not retaining its black colour, the proportion of it must be increased in the following operations till a residuum be left which preserves a tinge of black.

The sulphuric acid should be diluted with an equal weight of water. Rupp and Westrumb recommend a larger proportion. This mixture is best made in a leaden vessel.

Our process is presumed to be made with 11 pounds of manganese, 22 of acid, and  $29\frac{1}{2}$  of salt.

After mixing the salt and manganese, they are introduced into the matrass, which is then placed in the sand-bath, when the sulphuric acid, previously diluted and cooled, is poured into it. The tube of communication is now fitted to the orifice of the matrass. The ascent of the water of the intermediate bottle into the tube of safety denotes that the openings are air-tight. This may be further ascertained, by presenting to them the moistened stopper of an ammonia bottle; for however small the portion of chlorine may be which escapes, it becomes manifest by a white vapour.

We may kindle the fire in the furnace before placing the matrass in the sand-bath, taking care that the heat is not so great as to expose the matrass to be cracked when set in it; or we may wait till the whole apparatus is arranged, before lighting the fire. The heat is then to be very cautiously raised, till the intermediate bottle ceases to be filled with yellow vapours, and till the conductor tube begins to grow warm. The fire must now be extinguished. An operation for the above quantities lasts from six to eight hours. We must not delay withdrawing the matrass from the sand-bath till the movement of ebullition be entirely calm. The tube of communication is to be unluted, and whenever the smell is somewhat dissipated, the matrass is taken out, and placed in a basket containing dry straw. It is emptied whenever there is no danger of cracking the neck with the heat.

During the operation, the part of the matrass exterior to the sand-bath must be covered with woollen cloth, pasteboard, or any similar substance capable of confining the heat.

The accidents to be feared in this operation are the boiling over, and concretion of the residuum. The former occurs during the heats of summer. It is also occasioned by the bad quality

of the manganese. It may be avoided in both cases, by diminishing the doses. To guard against the obstruction of the tubes, which might arise from the boiling over, they must be made of sufficient magnitude. If, however, through inadvertency, the intermediate phial should be filled, so as to make it doubtful if the mixture can pass into the receiver, the matrass ought to be immediately removed. For if the mixture contained in it passes into the receiver, yarn turned through the liquor would take a yellow colour, which must be removed by means of sulphurous acid diluted with water.

The concretion of the residuum, which exposes the matrass to be cracked during the emptying, may be occasioned by three causes: the first is, too small a proportion of manganese; the second is, a lower temperature of the atmosphere than seven or eight degrees, (about 46° F.;) and the third is, keeping the matrass in the sand-bath some time after the operation, which happens when the heat has been pushed too far. The causes being pointed out, it is easy to avoid them.

As the temperature approaches that of freezing water, the gas occasionally takes a concrete form in the conductor tube, so as to obstruct it. To prevent this misfortune, very wide tubes must be employed.

Let us now turn our attention to the receiver. On adjusting each tube, care must be taken to cover it with water, and to extract all the air. This is done by means of a syphon introduced into the side opening, from which the water is expelled by blowing forcibly into its upper extremity.

The receiver being furnished with its tubs, and these being covered with water, with the exception of the upper one, we adapt the conductor tubes, passing them through the free space between the upper and lower tubs and the side of the receiver, and through an opening made in the board, which closes in the middle tub on the same side. This opening must be exactly shut as soon as the tubes are arranged. Lastly, the receiver is filled with water, which is not to be emptied again unless when repairs are to be made: care must however be taken every morning to evacuate the air which may exist under the upper tub, when the pipe just mentioned has not been placed in it.

From the arrangement of the tubs and the conductor pipe, it is obvious that the gas always arrives beneath the lowest tub,

and the liquor must consequently be strongest at the bottom of the receiver. From this place also it must be drawn off, for which purpose we adapt to the receiver a pipe (fig. 2. Q.) of wood, sand-stone, earthenware, or porcelain, which penetrates to the bottom, and whose upper end is on a level with the edges of the receiver. The liquor is run off by plunging a syphon into this extremity, the longer branch of which terminates in the water of the *tub of immersion*, (fig. 2. R.) In proportion as the liquor flows out of the receiver, care is taken to replace it by the addition of water or spent liquor. (NOTE N.)

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### CHAPTER III.

#### *Of Leys.*

THE defective manner in which leys are usually drawn, is the most frequent, most powerful, and yet the least suspected cause of the weakening of the substances subjected to bleaching. This part of the art, practised at all times, important both by its bad effects when ill conducted, and by the economy which it introduces into bleaching, when suitably performed, has received in modern times very little amelioration; yet it has acquired considerable improvements from more recent researches, especially those of Welter and Widmer.

It is necessary to know the exact quantity of alkali employed in each ley, so as to be able to graduate its respective force, and to proportion it to the quantity and nature of the materials to be bleached. Since the wood ashes, sodas, and the different species of potash made use of, are composed of a mixture of earths, salts, and alkalies, their weights indicate nothing; nor is the areometer a more faithful criterion, since the salts mixed with the alkali also act upon it. Hence its indications are more delusive as the proportions of the mixtures vary, not only in the different species, but as they are not constant even in any one.

Home,\* aware of the necessity of estimating exactly the strength of leys, attempted to determine the quantity of alkali

\* Essay on Bleaching.

contained in the different substances employed by the bleachers, by saturation with an acid. He thus assigned the order which they ought to hold relative to their quality, and he has explained the nature of the substances found mixed with the alkali, very ingeniously making allowance in his experiments for the imperfection of the means of analysis then known. But his results have not the precision of those since published. Long afterwards\* employed, for appreciating the real alkali of potashes, the comparative precipitation of a certain weight of alum, by pure potash, and by the potash under trial. Notwithstanding the precautions which he suggested for removing the causes of uncertainty attached to this mode of testing, he was not able to give it either sufficient accuracy or simplicity.† Lastly, Vauquelin took the task in hand, exhibiting the proportions of the substances found in several species of commercial potashes. He estimated the proportion of alkali, by saturating with a nitric acid, of a very determinate degree of concentration, the potashes submitted to examination, and by comparing the quantity of acid necessary to its saturation with the pure potash which it had required.

It is obvious, that since, in the art of bleaching, the alkaline parts alone are of use, the value of potashes are to each other as the quantities of acid necessary to their saturation; and consequently we become acquainted with that whose employment is most advantageous, by comparing the price of each species with the quantity of alkali which it contains. On these considerations, Vauquelin constructed the following table:—

At the time of making his experiments, the potashes of

America, containing	0.743,	was worth	70 livres.
Pearl-ashes	„ 0.656	„	60
Dantzic	„ 0.524	„	57 l. 10s.
Treves	„ 0.625	„	55
Russia	„ 0.670	„	55
Vosges	„ 0.385	„	35

Hence he concluded, that if the consumer wished to fix the prices which he should give for each potash, according to the alkali which it contains, taking for a standard the one which

\* Ann. de chimie, tom. vii.; and Treatise on Bleaching.

† Ann. de chimie, tom. xl.

the above table presents as most advantageous, 'he would have,—

1.	For the potash of Russia . .	55 livres.
2.	„ America . .	61
3.	„ Pearlashes . .	54 liv. 3 sous.
4.	„ Treves . .	51 6
5.	„ Dantzic . .	43
6.	„ Vosges . .	31 12

He justly observes, that the data of these tables are subject to variations, which fraud may increase; but they may serve in all circumstances as terms of comparison.

The testing of potashes, is useful, therefore, both for determining their commercial value, and as a guide in their subsequent employment. As the trials must be frequently repeated, it is important to have a simple manner of doing it; and under this point of view, we know none preferable to that of Welter. The process pointed out by the general administrators of gun-powders and saltpetres,\* though better adapted to the end which they proposed, is not so easy of execution.

We here give the process of Welter exactly as he practises it.

The principle of the testing is saturation with an acid. But to render the different trials comparative, the acid must be of a degree of concentration which is uniform, and easily ascertained. Sulphuric acid, diluted with water till it is brought to a determinate point of concentration, answers well. By saturating a certain weight of this dilute acid with a fixed weight of fine pure chalk, dried by the heat of boiling water, the standard may be fixed. This acid is the one most readily to be had, and whose constitution is most uniform. The chalk selected for determining its concentration is a substance equally common; it does not present the difficulties which occur in procuring pure potash, and the temperature of boiling water, employed for drying it, can be very easily observed with precision. To avoid the embarrassment attending the preparation of standard acid, a quantity of it sufficient for the trials of many years may be made at once.

Were these analyses made on pieces of potashes taken at random from the barrels, only ambiguous results would be got,

\* Ann. de chimie, tom. xli.

because in the same barrel there are often different qualities. The experiment should be made, therefore, only on solutions prepared on the great scale as leys, and always with the same weights of alkali to the same number of measures of water. The most expeditious manner of making these solutions in the cold, is to suspend the potash at the surface of the water in a vessel of iron pierced with a great number of holes, or formed of coarse iron wire. They should not be drawn off till we are certain that the whole potash is dissolved, and till by agitation the liquid is rendered uniform.

Besides these circumstances, the assay of potashes requires slips of paper stained with litmus, or any other colour equally sensible to acids, as that of mallows, radishes, &c. We should also procure a glass rod, a small glass measure, and lastly, a tube having as many times the capacity of the small measure, as measures of water have been employed to one hundred-weight of potash.—(See Plate II.)

We fill the tube with the solution of potash, and transfer it into the goblet. We next fill the same tube with the test acid, which is also poured into the goblet; we agitate with the glass rod, and then draw a trace on one of the slips of stained paper with the extremity of this rod moistened with the mixture. If the trace do not become red, we add to the goblet a small measure of the test acid, stir, and then make another trace on the paper, alongside of the former. If the colour of the paper be not now changed, we add one measure of acid more, and continue thus till the last drawn trace is red.

If we wish to compare the qualities of several potashes, it is obvious, that we must regard as the best that which has required the greatest number of measures of acid to produce a red streak, since it is the one which saturates most acid. It is also obvious, that we might express numerically the qualities of the different species of potash, representing them by the number of measures of acid which each of them has saturated; which amounts to counting the traces formed on the paper in each trial, taking the first for as many as the tube contains of little measures, and adding unity for each of the following marks till the last, which we should not reckon, because its colour indicates that we have passed the term of its saturation.

To obtain a suitable variation of the leys, it is convenient to

have solutions of potash of an uniform strength, one for example with which an equal number of measures of test acid and solution of potash are required to produce saturation. But whatever be the value of a potash, its solution may be brought to this point, by adding to it, for every hundred-weight of alkali, as many measures of water, as there were measures of acid required, to effect saturation on the quantity primarily employed. Hence the number of measures of water forming the solution, ought always to be equal to that which expresses the standard (*titre*) of the potash.

If in an assay it should happen that the first trace was red, it would be necessary to add measures of the solution instead of measures of acid; and hence potash should be added to the solution to bring it to the fixed degree of concentration.

To make this more clear, suppose that we have employed 50 measures of water to dissolve one hundred-weight of potash, (consequently the tube contains 50 times the small measure,) and that we have 8 traces on the stained paper. The first counting 50, each of the following 1, and the last being red, we would say that the potash is of the standard 56; which would denote, that to bring the solution to the fixed degree, (in this case 50,) we must add as many times 6 measures of water as we have employed in hundred-weights of potash; and employing potash taken from the same cask, we should use 56 measures of water for the solution. An assay made on opening the cask, is sufficient for the whole period of employing that potash, remembering to put, every time a new solution is made, as many measures of water as the standard indicates. (NOTE O.)

The degree of concentration of these solutions does not allow them to be employed directly in the leying. Only such a number of measures is taken as is necessary to give them sufficient strength, when diluted with the water which fills the boiler and the bucking tub, and for them to have the quantity of alkali suited to the weight of the substances to be bleached. But before pouring the alkali into the boiler, it is advantageous to render it caustic; for it has been proved, (*Ann. de chim.* tom. vi.) that in this state alkalies dissolve a fourth more of colouring matter than when they are carbonated. The almost general practice, however, is to ley in a mild state. It has even been pretended, in some houses, that the lime employed to render the



alkali caustic, injured the stuffs. The observations which we have collected satisfy us, that this effect must be ascribed solely to the increased energy acquired by the alkali, the consequences of which may be prevented by a diminution of its quantity.

To perform this operation, the lime newly slaked is put into a large tub, the solution of potash is poured over it, they are stirred together, and, after settling, the clear liquid is to be decanted off by means of a syphon. The residuum is then to be washed away two or three times, and the washings added to the ley.

One part of lime is sufficient to render two parts of potashes caustic. These proportions ought, however, to vary with the qualities of the potashes; and it is proper to ascertain that the proportion of lime is not too great, because the property which this substance possesses, of precipitating the colouring matter held in solution by the alkalies, (*Ann. de chim. tom. vi.*) may render an excess of it injurious. On this account, some solution of potash is to be mixed with the liquor floating over the lime, in the tub in which the potashes are made caustic. If it become turbid, it contains lime in solution, and solution of potash must therefore be added, till it no longer yields a precipitate.

We might probably apply this property of lime with advantage, to carry off from spent leys the colouring matter with which they are charged, and render them once more fit for bleaching, by adding the proportion of alkali necessary to replace that with which the stuffs remain imbued, so as to raise the leys to the suitable standard. On the small scale, yarns have been completely bleached, by employing in this way the very same alkali in all the leys. It may be likewise beneficial, especially in places where fuel is cheap, to evaporate the spent leys, and to calcine the residua so as to destroy the colouring matter. But these operations need only be performed on the first leys, which are more concentrated than the last.

According to the experiments of Kirwan\* the use of alkaline sulphurets might be tried. They have indeed the inconveniences of producing spots in places which come into contact with metals; but these will disappear by employing in the last leys

\* *Annal. de chimie, tom. vi.*

an alkali free from the sulphurets, or by passing them at the end of this bleaching through an acidulated water. The following is the order in which this celebrated chemist has classed, according to their energy, the substances possessing the faculty of dissolving the colouring matter of flax: 1. The alkaline sulphurets; 2. Caustic potash; 3. Caustic soda; 4. Carbonate of potash; and, 5. Carbonate of soda. Lime water appeared to him to dissolve but a very little of it, which he ascribes to the small solubility of the lime; but independently of this cause, it is not probable that lime, which forms an insoluble combination with colouring matter held in solution by potash could of itself dissolve it. Kirwan observes, that sulphur did not augment the solvent faculty of lime. Higgins, however, has stated, that there is a remarkable economy in employing sulphuret of lime in bleaching. Trials on the small scale have not had the success that O'Reilly announced.—*Journal des Arts*. (NOTE P.)

The sulphurets present two inconveniences, which must greatly diminish the benefit which their solvent faculty promises. One is, to deteriorate rapidly boilers and metallic instruments containing them; another is, to waste a considerable quantity of the chlorine, if the washings have not taken it completely out of the matters that are bleaching.

The colouring matter acquires the property of being dissolved by the alkalies only in the successive operations, between every one of which whatever has become soluble ought to be removed. Experience has proved that these steps are necessary to obtain a fine white, not subject to vary; a white which cannot be attained at a single operation.\* The alkali deemed necessary to dissolve the whole colouring matter of the substance we are bleaching, must therefore be divided into a certain number of leys; and as it should be proportioned according to the quantity of this colouring matter presumed to be present, less of it may be employed in the last leys than in the first.

The most general manner of leying is the following:—

The large tub is so placed, that its bottom may be near to, and on a level with the edges of a boiler, which is somewhat sunk into excavated ground, to avoid too great an elevation of the tub. A little above its bottom this is perforated with a

\* *Annal. de chim.* tom. xi.

hole, into which is fitted a small tube, that conducts the ley into the boiler. The stuffs to be bleached are arranged in the tub in horizontal layers. The boiler is then filled with water, which is poured into the tub after closing the pipe that leads into the boiler; and this operation is continued till the water stands in the tub a little above the goods, taking care to mingle with each boiler-full of water a number of measures of solution of potash, equably divided, so that with the last boiler-full the whole alkali intended for the ley shall have been expended. The boiler being equably filled, the fire is kindled, the pipe of communication is opened, and the water is kept at a uniform height in the tub, by lifting it with a copper pail or bucket from the boiler, and pouring it into the tub. When the ley (thus continually lifted into the tub in proportion as it flows into the boiler) has begun to boil in the caldron, the operation (of bucking) is prolonged more or less, according to the kind of matters that we bleach, and the period of bleaching at which they have arrived. The leying being finished, it is allowed to flow off by a stopcock fitted to the bottom of the boiler; water is then poured into the tub to cool it, and expel the remainder of the ley, after which the tub is emptied.

Since the tub contains several times the capacity of the boiler, and since, independently of the time which a considerable volume of water takes to acquire a high temperature by the mixture (in rotation) of a small quantity of heated water, the ley is continually cooled by the transfer from the boiler into the bucking-tub, the ebullition in the boiler must be but very slowly brought on. However long continued the leying may be, the temperature cannot be carried higher than  $72^{\circ}$  or  $73^{\circ}$  (about  $195^{\circ}$  Fahr.) in the tub. From this arrangement it follows, therefore, 1. That a great body of water must be heated, in order that the substances bleaching may be equably impregnated with the ley; and, 2. That we can give the leys only a heat inferior by several degrees to that of boiling water. Hence the length of the operation, as also the waste of combustibles, and the great labour: nor can the term of  $80^{\circ}$  ( $212^{\circ}$  Fahr.) be obtained. Several phenomena, however, and especially the superiority found in patterns bleached in boiling leys, show how advantageous the temperature of ebullition would be.

From these considerations Widmer contrived to place directly above his boiler a tub, whose bottom was merely a strong lattice work of wood. In the middle of the boiler there is a pump which raises the ley to the top of the tub, where it is diffused by four pipes equal to the radius of the tub, and which are turned circularly by a movement adjusted to the arm (lever) of the pump. The ley is thus equably dispersed on the surface of the goods; it filters through them, and falls into the boiler. Far from being liable to cool, it preserves its temperature in this passage, because the goods are heated by the steam rising from the boiler, which cannot escape except by passing through their interstices. Two thermometers placed in an apparatus, where the boiler was two yards in diameter, one at the base and another at the top of a tub two yards high, constantly marked the same degree of heat. In three hours of an uninterrupted flowing, they both indicated  $80^{\circ}$ , ( $212^{\circ}$  Fahr.) In the first trials, Widmer made use of a tub whose height was two yards, and whose diameter, equal to that of the boiler on which it stood, was only two feet eight inches. The ley was drawn off by a stopcock adjusted to the bottom of the boiler, and it was poured in with a bucket quicker than it could run completely away. That remaining on the top of the goods boiled strongly some minutes after the boiler was in ebullition, notwithstanding the small surface which this apparatus presented to the vapour, the cooling which the ley must have experienced in getting back into the boiler from the top of the tub, and the distance between this point and the boiler. By this method we may communicate to goods a heat superior to that of boiling water. The thermometers of the large apparatus rose to  $84^{\circ}$  ( $221^{\circ}$  Fahr.); but as soon as they passed the boiling point of water, the pump could no longer raise the liquid; and we do not know how far it may be right to ley at higher temperatures. To prevent the pressure of the steam from stopping the working of the pump, Widmer next established four pipes, which opening a communication between the upper part of the boiler and that of the tub, gave a free outlet to the vapour.

This apparatus unites the advantages of leying in much less time, at a boiling heat, and with less consumption of fuel; for instead of having to heat a ley incessantly cooled by the trans-

fer, and which occupies the capacity of both the tub and the boiler, the latter alone is filled, while the heat is preserved during the running by the agency of the vapour.

Nearly 400 pieces, of from 23 to 24 yards each, may be leyed at a time in an apparatus of the above dimensions. The longest leying lasts six hours: it consumes five measures of coals. Its efficacy is sufficiently proved by the uses to which the goods of Widmer so bleached are applied, since there can be no more delicate test for white, than the clearing the madder grounds of printed calicoes; and it has also diminished the number of operations to which he subjects the goods. We have had occasion ourselves to ascertain these good effects on cotton cloth; and we believe that they will be experienced on applying this method to the bleaching of linen webs. (NOTE Q.)

Bosc has asserted in a paper,\* on which we have some reflections to offer, that it was prejudicial to the action of the alkali to water the goods continually; an idea which he founded on his philosophical notions of bleaching. According to him, "the solution of the colouring particles in the alkali is a true combustion, effected only on the colouring matter, because it is combustible at a lower temperature than the fibres." Our only business, therefore, is to raise sufficiently the temperature of the steam, so as to operate by its decomposition the combustion of the colouring particles, which thus become soluble in the alkali.

When water is decomposed by means of charcoal at a much higher temperature, there are produced carbonic acid and an inflammable gas, holding carbon in solution; but the charcoal which has not entered into a gaseous combination has not become more soluble in alkalies. This observation would be sufficient to prove that the explanation of Bosc is not founded on the received theories.

He makes Lavoisier say, that at 85 degrees of Reaumur, (about 223° Fahr.) "water forms a permanently elastic gas." This illustrious chemist styled permanently aeriform fluids, those which preserve this state notwithstanding changes of temperature and pressure. The vapour of water formed at 80° (212° F.) under the ordinary pressure of the atmosphere, differs from that formed at 85° only in being more dilated, and resisting a higher (less) pressure.

\* Bulletin de la société d'encouragement, pour l'industrie nationale. Germinal, An. xi.

He certifies, that in the apparatus which he describes, the heat is carried beyond the 100th degree of Reaumur; but at nearly 17 degrees above the term of ebullition, (250° F.) steam acquires a double elastic force. His vast apparatus should therefore be able to resist an effort superior to two atmospheres. He should have bethought himself of determining the thickness necessary to the great boiler which is to furnish this vapour, and have showed us by what means he could fix down the different parts of the apparatus to the masonry.

In making a comparative calculation of different modes of bleaching, he regards as a matter of indifference the employment of chlorine without mixture, or combined with potash and lime. We shall afterwards see how far this position is right.

When the results of different methods are compared, especially on cotton, where some days' exposure on the grass forms a part of these methods, and when it is not the object to attain the most perfect white, it is easy to be led into error, because all these methods readily yield a white, with which people may often be satisfied.

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#### CHAPTER IV.

##### *Of the Immersions in the Solution of Chlorine.*

If linen or cotton yarn is to be bleached, for its immersion in the chlorine, we may place near the receiver a tub of the same size, but a foot lower, (fig. 1, 2, A.) It is to be two-thirds filled with water; the liquor of the receiver is then run into it by means of a syphon, as we have explained, agitating meanwhile, but without raising air bubbles. The hanks are arranged in a basket of the same height as the tub of immersion, so as to form two layers in it, leaving 8 inches empty. The basket should contain from 220 to 330 pounds of yarns. This basket is then raised by means of a crane or other equivalent machine, and plunged into the immersion tub; from which it is withdrawn, and replunged into it continually, so as to renew incessantly the liquid which moistens the yarn. As soon as the liquor is observed to be weakened, the basket is raised above the tub, and fresh liquor is run in from the receiver. This process is continued until the liquor retains its strength, not-

withstanding the repeated immersions of the yarn. This first operation usually lasts two or three hours.

Instead of heaping the yarn in baskets, it may be plunged much more freely in the liquor, by hanging it at two rods, which pass through the middle of the hanks, and are supported by a frame of the same size with the immersion tub. There is then no danger of the yarn being bleached unequally. Less of it, indeed, enters at a time into the tubs. The mode of working is in other respects the same.

Chlorine weakens and even destroys yarns, as leys do, if it be employed without precaution. Hence, when yarn is put into a very strong solution it soon loses its tenacity. But it is very easy to avoid this occurrence, by not dipping the yarn till the liquid which comes out of the receiver be well mixed with water, or be a dilute liquor with a supportable odour. In this state of concentration, the chlorine does not attack yarn, though plunged in it even for several days. We must not rest satisfied with so vague a manner of judging, especially if we wish to compare together several effects.

From the outset of his operations Descroizilles made use of a solution of indigo in sulphuric acid, to estimate the comparative strength of his liquors; and he has since published a description of the instrument which he contrived for this purpose.\* The solution of indigo ought to be prepared with seven parts of concentrated sulphuric acid, and one part of fine indigo. These two substances are mixed in a small matrass, which is plunged for a few hours in water slightly tepid; and the solution is then mixed with 992 parts of water.

The strength of a liquor is judged of by the quantity of it requisite in order that the colour of a stated measure of this solution, in which the indigo forms 1-1000th, be destroyed or turned to a yellow hue. This trial is conveniently made with a measure glass and a goblet, similar to those pointed out for the trial of potashes. (NOTE M, latter part of.)

For a first immersion, the liquor may be of such a strength that one measure of it shall deprive of colour from one-half to two measures of solution of indigo. If the odour gives annoyance, it may be diminished by diffusing some chalk and water in

\* Journ. d'agriculture et des arts, tom. i.

it. We have ascertained, that this easy method of obviating the inconvenience of the smell, does not perceptibly impair the energy of the liquor. The strength and duration of the immersions which follow the first, are progressively less. Their number varies also according to the fineness and quality of the yarns. In general, they are limited to between five and nine.

Too weak a liquor should not be made use of, from fear of weakening the yarn; for its deficiency of action cannot be compensated by a greater number of immersions. It is easy, moreover, to avoid any accident from the liquor, by never omitting to try its strength. Attention must also be paid, not to let the yarn that is impregnated with it dry in the air; it is thereby injured, although no inconvenience happens while it is wet.

The bleaching of piece goods requires the same precautions. The finer the cloth, the more economical, because it consumes less liquor; but to execute it commodiously, there must be, instead of a single tub of the size of the receiver, four tubs sufficiently large to contain each from ten to twelve pieces, 26 yards long. These tubs, arranged one after the other, near the receiver, are each surmounted by a reel or winch. In front of the first tub a table is placed, to which are attached at their corners the ten pieces that are to be immersed together. After bringing the liquor to the requisite degree, the end of the last attached piece is thrown upon the winch of the first tub. A workman immerses the pieces with a rod, in proportion as they pass over the winch, which is turned by a child. The end of the last piece is tied to a cord fixed to the framework of the winch, in order that this end, which enters last into the tub, and which finds the liquid now weakened by the pieces to whose train it is attached, may enter first into the second tub, and that the end which has been first in the preceding may, by passing last into the next, be placed in the same circumstances as the other. By giving this rotation to the goods in the tubs, with a view of changing them, and by successively passing each end first, they whiten very equally. When the pieces have been passed from the first into the second tub, new ones are introduced, which pass into the second as soon as the former have entered the third, and which pass in their turn into this, when the preceding pieces are in the fourth. At the same time, fresh pieces should be put into the first two tubs; so that as soon as the pieces shall have travelled



from one tub to another, others may enter immediately into the former. When they have arrived at the fourth, and have remained the requisite time in the liquor, they are piled up on the winch to let them drain, then turned over on a wheelbarrow to be carried to wash. Whenever the pieces are taken out of a tub, the liquor of it is tested, that it may be restored to the proper degree before introducing fresh pieces into it. Care should be taken to plunge the pieces thoroughly, and not to let any of their parts float above. The number, the strength, and duration of the immersions, vary with cloths, as with yarns.

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## CHAPTER V.

### *Of the Washings.*

WHOEVER projects an establishment should examine if the place where he proposes to erect it, unites the advantages of fabrication, commerce and carriage; but, above all, he must have pure water at command; for, without this condition, he will not succeed in obtaining a fine white. Muddy water, which leaves a blackish deposite, may however be employed with success; but that whose deposite is yellow, gives always an unfavourable shade. These observations are particularly applicable to the bleaching of cotton, the white of which should have the greatest lustre.

Immediately after each operation, we must, by a careful washing, discharge from yarns and stuffs the liquor with which they are impregnated; because, if it were carried into that of the next operation, it would neutralize a portion of it, and thus impair its action. This precaution, moreover, adds much to the perfection of the white.

To wash linen or cotton yarns, a workman takes a hank in each hand, plunges them in the water, agitates, withdraws, and replunges them for three or four times, seizing the hank each time by a different point. He then puts the two hanks together, wrings them, and throws them down.

The washing of piece goods requires more apparatus in order to be well executed. They are pretty generally washed by hand, and beat with a rod or a mallet; but this method is im-

perfect, especially because of the inequality of the washing. In some establishments machines are employed, which accomplish this object better. We are acquainted with none preferable to that of the celebrated manufacture of Oberkampff, of which he has had the kindness to impart the knowledge to several bleachers. It consists of a strong beetle or mallet, which strikes the pieces arranged on a circular table, moveable round a pivot. A description, detailed enough to guide to its construction, would require too much room for us to give it a place here.

We may, however, obtain a pretty complete washing, sufficient for the most part of goods, by making use of two wooden rollers, placed one above another on frames, set in the direction of the breadth of a river. Their length is 1 foot 4 inches, the under one is 1 foot 7 inches in diameter, while the upper is only 1 foot 4 inches. The latter is fluted parallel to its axis, the depth of each furrow being nearly equal to one-half of the ridge. At each extremity it has a pivot, fitted to a groove cut in the frame, (support.) These pivots are not fixed, hence this cylinder can rise freely above the other. The surface of the under roller is smooth; and it carries a handle at one of its pivots. When we wish to wash goods by its means, we throw the piece into the water, laying hold on one of its ends, and putting it between the two cylinders. On turning the winch, the cloth passes between them, pressed by the upper one, which, at every groove receives a small stroke, and communicates it to the cloth in its tumbling round. Pieces passed in this way five or six times successively, are very well washed.

To moisten goods, or to wash them slightly, we may also employ a species of reel (winch) with four leaves, placed on a river, like the rollers. The piece whose end is laid on the reel is thrown into the water, and, turning on the reel, the piece passes over it, and falls on the other side into the water. If it be rapidly enough turned, and if the pieces be thus passed several times, they will be tolerably well washed by this simple means.

What has now been stated shows the advantages of arranging the workshops as near as possible to the water placed at our disposal. (NOTE R.)

## CHAPTER VI.

*Of the other operations of Bleaching.*

THE bleaching of goods commences by leaving them for some time in tubs full of water. In a few days a fermentation commences, which promotes the separation of the colouring matter, and particularly of the paste with which weavers imbue their webs. This operation, which is called *ungumming*, may, without injury, last for eight or nine days, at mean temperatures. It may be longer when the air is cold, and ought to be shorter in summer, because it is to be feared that fermentation, pushed too far, would affect the texture of the goods. Old leys are also used for this purpose; but the experiments of Home prove, that it is more advantageous to employ only pure water.

As to yarns, it is sufficient for them to be steeped for two or three days.

If the moist grey yarn, on coming out of the ley, be piled up, it gradually heats, and eventually takes fire; but if it reaches only the animal temperature, it is not perceptibly weakened; the slight combustion which it thereby experiences even contributing to the effect of the leys. If it be shut up in the dark, however, when ill dried, it is speedily destroyed.

When no more greyness remains in linen yarn, or linen cloth, which commonly occurs after the fourth immersion, it is passed into water acidulated with sulphuric acid. For this purpose, into a small tub containing water, sulphuric acid is poured, till the mixture has assumed a degree of sourness approaching to that of lemon juice. Into this the yarn is dipped, handful after handful, so as thoroughly to imbue it. It is then thrown into another tub large enough to hold 1200 pounds of it, in which it is left for about 15 or 20 hours before being removed. A longer continuance, of two or three days, for example, can do no harm, provided care be taken that no portion of the yarn rises out of the acid. As to piece goods, they are attached end to end, and passed by means of a reel through large tubs full of acidulous water. Linen yarns and cloth are passed three or four times through the acidulous water, making it progressively weaker. It is sufficient for cotton goods and yarn to be passed once. The quantity

of acid employed in the first liquor is 18 pounds, for 1320 pounds by weight; and this proportion is diminished at each subsequent operation.

Great pains must be taken to wash perfectly before and after the acidulous water, otherwise a fine white can never be obtained. It is no less important to prevent the yarns or cloth impregnated with acidulous water from remaining long exposed to the air; for as the water evaporates, the acid becomes concentrated, acts on the fibre, and destroys it.

The acid dissolves the iron which in the course of the operations had been deposited on the stuffs, communicating to them a faint yellowish tint. In proof of this, the prussiate of potash occasions, after some time in the sour, a blue precipitate. But is the action of the acid confined to the above use? If it be, why repeat this operation four times, and apply a ley between each of them, while for cotton, equally exposed to be stained by the ferruginous deposite, a single sour is sufficient?

In Flanders, Holland, and Ireland, the bleaching of cloth by the ancient methods is accelerated, by letting them stand for several days in the acidulous liquors. Sour milk is commonly employed for this purpose; sometimes, also, bran or rye-meal is mixed with the cloths, and the liquor of the tubs becomes sour from fermentation. It was long believed that the fermentation itself promoted the bleaching; but it is now well proved that it is the acid alone which acts. Home has satisfied himself, that the vegetable and mineral acids may be substituted for milk and rye-meal; that sulphuric acid, however, combines most advantages; that muriatic and nitric acid produce the next greatest effect, which effect is aided by a gentle heat: He assures us, that sulphuric acid does, in five hours and less, what could be obtained only in five days with bran or milk. To these substances he also makes the serious objection, that they frequently run into putrefaction, and thus affect the fabric. We may hesitate the less to substitute water acidulated with sulphuric acid for milk or rye-meal, as this change has been long adopted in England, and in several French bleach-works.

Notwithstanding all these operations, the thread has not yet got all the whiteness of which it is susceptible. There remains a matter insoluble in acids and alkalies, which is removed by powerful washings in water frequently repeated, and by some

days' exposure on the grass. There is a certain yellowish tint, which is more effectually destroyed by the action of air and light, than by that of chlorine. In general, yarns of a yellow colour bleach with more difficulty than those of a grey hue bordering on brown. For those, it is right to lengthen somewhat the exposure on the ground.

For giving softness to yarns, some pounds of soap are added to the last leys. Immediately afterwards they are laid out on the green, on being lifted from which they are washed with great care; for if they retain any soap, their white might change. In linen webs, the selvages being of a denser texture than the rest, preserve for a longer time a tint, which can be completely removed only by reiterated washings and soft soap. It is the same with all the places on the body of the cloth where there are broken threads repaired during the manufacture. These constantly preserve a black hue, which yields only to rubbing with a hot solution of soap, of greater or less strength. Some persons are in the practice of treading the cloths in tubs along with this solution, one or two times, towards the end of the bleaching. This operation is performed with the feet, tramping more or less according to the hardness of the web. To cleanse the cloth completely, it is soaped by hand in tubs, whose edges, instead of being perpendicular to the bottom, are turned considerably outwards, forming an inclined plane, on which the workmen rest their webs, so as to rub them more conveniently. If the goods are almost quite cleared by the two treadings, a single rubbing is sufficient to bring the selvages to the same tone of white as the rest of the piece; most frequently two are given, especially to webs of a dense texture, or of a coarser yarn. Occasionally they are obliged to rub, even separately, the spots where the black threads are observed. All these manipulations, by cleansing thoroughly the goods, give them, moreover, a certain pliancy, and that marrowy feel which is in request. The whole of the soap that may possibly remain is removed, by exposing them on the field, and washing them several times in limpid water. The soaping does not begin till the webs have passed once through the acid, care being had to lay them down on the grass on their quitting each operation, and to water them on it. They are next washed and lixiviated. The acid and soap are alternated, till a perfect white be formed.

Cotton stuffs do not present the same difficulties. The black threads are easily cleared towards the end of the bleaching, by soaping the places where they are observed; but the selvages whiten as rapidly as the body of the web; and exposure on the green may be dispensed with.

When a perfect white is obtained, the blueing is given in the following way:—

The most beautiful azure-blue (*smalt*) is selected, the colour of which proceeds from oxyde of cobalt reduced to a very subtile powder. It is diffused through a little clear water. Some of the water thus charged is drawn off, and passed through a silk searce, into a small tub filled with the most limpid water; and when the workman judges, by a trial made on a handful of thread, that the water is sufficiently charged, he passes through it all the thread in succession, squeezing it, and taking care to add blue from time to time, to keep the shade uniform. The yarn is now carried to the wringing frame, and then dried in the open air.

The preparation is the same for piece goods. They are wrung at the peg, and dried. As to gauzes, lawns, and some other cotton stuffs, a little starch is added to the water containing the azure-blue. Cambrics are usually passed twice through the blue, letting them dry between each operation.

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## CHAPTER VII.

### *Number and Order of the Operations.*

SUPPOSE there is a solution of potash made in the proportion of 40 measures of water, each weighing 16 pounds, for a hundred-weight of potash, and 1250 pounds of thread.

The linen or hempen yarns having been steeped in water for three days, are to be well washed, and arranged in the ley-tub.

*First ley;* 20 measures of solution of potash, three hours of boiling. The ley, on cooling, becomes thick like a jelly.

*Second ley,* for completing the removal of as many of the colouring particles as possible. This ley contains 10 measures of solution; and the boiling lasts for two hours.

*Washing*, to carry off the ley and the colouring particles which it has dissolved.

*First immersion.* Liquor at  $2^{\circ}$ ; that is, of such strength that one measure of liquor discolours two measures of solution of indigo. The immersion is continued till the yarn no longer weakens the liquid, after it is restored to its standard strength.

*Washing.*

*Third ley*; 12 measures of solution; three hours of ebullition.

*Second immersion.* Liquor of the same strength as the first.

*Fourth ley*; 8 measures of solution; two hours of ebullition.

*Third immersion.*

*Washing.*

*Fifth ley*;  $5\frac{1}{2}$  measures of solution; two hours of boiling.

*Fourth immersion.* Departing from this point, the liquor is brought down to  $1^{\circ}$ .

*Washing.* At this period the white is usually manifest.

*Acidulated water.*

*Washing.*

*Sixth ley*;  $5\frac{1}{2}$  measures; two hours of ebullition.

*Exposure on the green* for six days.

*Washing.*

*Fifth immersion.*

*Washing.*

*Acidulous water.*

*Washing.*

*Seventh ley*;  $4\frac{1}{2}$  or 5 measures; one hour of ebullition at least.

*Sixth immersion.*

*Washing.*

*Acidulous water.*

*Washing.*

*Ley and soap*; 3 measures of solution. To this 8 pounds of black soap are added; and the solution is heated till the hand cannot be tolerated in it. When the soap has penetrated thoroughly, the process is stopped.

*Exposure on the grass*, three days.

*Washing.*

*Blueing.*

After this operation, the bleaching is finished, the thread is wrung out, and is set to dry.

The operations are the same for linen cloth, only they must be preceded by the ungumming. There may also be run upon them, before the first ley, hot water, to which no alkali is added; an operation which lasts three hours. If the goods be not sufficiently whitened, the bleaching must be continued in the order indicated, setting out from the last ley.

The cotton cloths are ungummed, (freed from the dressing,) then receive the hot water, and the operations prescribed for yarns down to the last immersion. At this time they are white. They are passed into blue acidulous water, and next dried. In the first immersion, the liquor should be of only  $1^{\circ}$ , and somewhat weaker for the subsequent ones. A few measures less should likewise be put in each lixivium. The black threads are soaped after the third immersion. For cotton in hanks, the same mode of operating is proper.

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## CHAPTER VIII.

### *Of the Different Preparations of Chlorine Liquor.*

IN the first experiments which were attempted on bleaching, though it was proposed merely to employ the property which chlorine possesses of destroying colours, yet potash was mixed with it, which seemed to accelerate its effect. It was soon perceived, that in order to obtain a uniform white, without weakening the cloth, the operations of ordinary bleaching must be imitated; the oxygenation of the colouring particles by a liquor weak enough to do no injury to the fabric, being followed up by the action of leys which serve to dissolve them.

Soon after the practice of the new bleaching had begun to be established, a liquor mysteriously talked of, was prepared at Javelle, which is still employed under the name of the lixivium of Javelle.\* It is a combination of chlorine with a certain proportion of fixed alkali. This liquor can be imitated by employing

\* Ann. de chimie, tom. ii.



the following proportions for the distillation and the alkaline solution :—Muriate of soda, 1193 grains ; sulphuric acid, 945 gr. ; oxyde of manganese, 465 gr. The gas disengaged from these materials is received in  $1\frac{1}{2}$  pints of water, in which 1860 gr. of common potash or soda have been dissolved. This liquor is to be diluted for use with 10 or 12 parts of water.

To diminish the offensive odour of the chlorine, Descroizilles mixed with it carbonate of lime or chalk.

A short time since, Tennant made a preparation for which he obtained a patent in England: it is a combination of chlorine and lime, or chloride of lime. This substance has the property of absorbing readily a great quantity of chlorine. To obtain this combination, it is requisite merely to pass the gas, as it is disengaged, through slaked lime till it be saturated. This lime is afterwards dissolved in a certain proportion of water; which solution is employed in bleaching. Its effect may be augmented by the addition of a little sulphuric acid.

To judge of the effect obtained from these different preparations, and of their relative utility, we must call to mind, first of all, the results of observations collected from the theory.

Oxygenated muriatic acid (chlorine) is composed of two elements, which are feebly united, and which are disposed to enter into other combinations; whence the easy oxygenation of substances exposed to its action. But this action is exerted with greater facility and energy when not impaired by any combination which the chlorine may have previously made. Thus, in the gaseous state, it acts with more energy than when it has been combined with water beforehand; and in that case its activity may be too great for the object proposed in bleaching. The action of the water, however, being very feeble, the liquid retains a lively odour, and there may be obtained from it its whole sensible effect, only retarded and modified at will, according to the concentration which is given it.

The alkalis exercise a much more powerful action on chlorine than water does, and thereby can give it a much greater condensation, repressing almost entirely its smell, which requires freedom of expansion, and solution in air. The above (alkaline) liquor is dissolved in a sufficient quantity of water to accomplish the intended object of obviating the inconveniences of too brisk an action. It produces its effect more quickly, probably because

the potash tends to form a more intimate and more energetic combination with the muriatic acid, while the colouring matter exerts its action on the oxygen.

The advantages presented by the lixivium of Javelle,—the chloride of potash or soda, are therefore—1. To require a less complex apparatus, for it is sufficient to employ a receiver containing the alkaline solution, in order to condense the chlorine gas, with the single precaution of plunging the conductor-tube to the bottom of the receiver, and receiving the gas under a tub ; 2. To repress almost entirely the suffocating odour of the chlorine ; 3. To furnish the agent of oxygenation, much more condensed, under the same volume, and consequently to render it of easier and less expensive carriage ; 4. lastly, To produce its effect somewhat more speedily.—Let us next examine the disadvantages of this preparation.

When a fixed alkali acts on the oxygenated muriatic acid (chlorine) the effect is not simple ; a portion of the oxygenated muriatic acid is merely condensed, retaining the proportion of its elements, and the properties dependent on the tendency which they preserve to enter into other combinations.

Another portion is decomposed ; and the result of the two new combinations which are established in its stead, gives from five to six parts of muriate of potash for one of chlorate of potash, a salt which contains nearly 0.38 of its weight of oxygen, to which it owes its characteristic properties. Now, the oxygen present in this last combination, in which it is accumulated, is so fixed down, that it can no longer attack the colouring particles, nor resume the elastic state by the action of light. The whole of the chlorine which suffers this transmutation of combination, is therefore lost for bleaching. Its quantity varies according to the condensation of the alkaline liquor which receives the gas, and it appears to increase when the liquor is kept ; probably temperature causes the results to vary.\*

We thus perceive that liquors, analogous to the lixivium of Javelle, ought not to produce in their agency on the colouring particles so much effect as the simple aqueous solution, which contains, under the same liquid volume, a quantity of chlorine gas equal to what has been condensed by the alkali.

\* *Essai de statique chimique*, tom. ii.

It has even been found, that by adding simply an alkaline solution to chlorine, its discolouring effect was diminished. Rupp has made decisive experiments on this subject. He employed a solution of indigo for comparing, by the quantities of which the colour was destroyed, the chlorine without mixture, with the same after adding to it different proportions of potash; but to avoid the uncertainty which might have proceeded from the action of the sulphuric acid on the potash combination, he decomposed the solution of sulphate of indigo by acetate of lead, thus rendering what he used, a solution of indigo in acetic acid. He made similar trials with an infusion of cochineal, which is still less liable to objections. It results equally from both, that in proportion as potash is added, the bleaching power of chlorine is diminished. The difference between the simple solution of chlorine, and that with which he had mixed most potash, was nearly one-fourth in favour of the former.

It is therefore proved, by theoretical considerations and direct experiments, that the addition of an alkali, when even it is not employed to condense the chlorine, impairs the effect which this ought to produce. But in the *lixivium of Javelle*, it raises the price of the liquor nearly three times higher. It is obvious, that these disadvantages ought to make the use of it be rejected in a manufacture where economy is an indispensable condition.

The chloride of lime has one advantage over the *lixivium of Javelle*, from the great difference of price between lime and potash or soda; and its state of condensation and desiccation, renders its carriage less expensive. But it has also the inconvenience of transforming a portion of the chlorine, and of containing chlorate, which cannot be indicated in this combination by nomenclature, which is precise only with regard to very uniform combinations: it appears even that the proportion of chlorate is considerable; for if, after expelling, by a slight degree of heat, the chlorine which has retained its properties, the remaining substance be examined, it is found no longer to produce discoloration; and if it be urged with a stronger heat in this state, much oxygen gas is disengaged. - Welter tells us, that in his comparative experiments, he had observed, that the gas condensed by lime produced only one-tenth of the effect which may be obtained when it is received in water. The use of the chloride of lime must therefore be disadvantageous; but it may be convenient for

certain purposes, from the facility of carriage and preservation, where the economy of the process is of secondary consequence. Under this point of view, it merits the commendation which it has received. (NOTE S.)

The addition of sulphuric acid to the solution of the chloride of lime, increases the effect, by the decomposition of the chlorate; but to produce this effect fully, a quantity of acid is required which might become dangerous.

These objections do not apply to the addition of chalk, which has been recommended by Descroizilles, of which he makes use in his elegant manufactory. Its value is very trifling; and although our experiments appear to prove that it somewhat lessened the total effect of the chlorine, yet this diminution is so small that it may be neglected. Hence, though the process with the simple solution of chlorine may be executed without inconvenience, there is no harm in employing the addition of chalk, so as to repress the greater part of the odour. We even recommend not to omit its use, whenever persons are not very well instructed in conducting the operations with the customary attentions which are required.

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## CHAPTER IX.

### *Of the Other Uses of Chlorine.*

THE property of discolouring and whitening which chlorine possesses, has met with several applications, which their analogy to bleaching, and their relation to the art of dyeing, induce us to enumerate.

When cloths have been printed with different mordants, they are passed into the madder, where the designs assume different hues, according to the nature of the mordants; but the (vacant) ground of these cloths also receives the madder colour. This colour is much less fast than that which has been fixed by the mordants; and it must be destroyed by means of cow-dung and bran, and long exposure on the grass. Nearly the same process is employed to destroy the yellow ground of printed goods which have been passed through weld to give the figures those hues which belong to yellow. At Manchester, the properties of chlo-

rine, modified by certain operations, which have not been made public, were speedily applied to that purpose.

Widmer and Haussman made some trials, each in his own way, from which it was ascertained, that a liquor, composed in the proportions which we have pointed out for the lixivium of Javelle, might be employed with success, but with the precaution of diluting it for use with a larger quantity of water. We shall state the result which Widmer has given of his experiments.

“When the cloth comes out of the madder, it is exposed for four or five days on the grass; it is then passed through a bath of cow-dung, after which it is laid down four days longer on the grass, as at first. It is now submitted to an immersion of about half an hour in the bleaching liquor, previously diluted with about 35 parts of water. After this operation, the cloth must be exposed for two days on the grass. It is then subjected to a new immersion, and exposed for other two days on the field. Betwixt each operation the cloth must be well washed and beetled. The exposure on the field, here prescribed, is understood to be during fine weather; for in bad weather it must be exposed some days longer. In general, the ground of a cloth which has been well maddered, in order to have fast thorough-proof colours, should be perfectly white after this manipulation.

“It appears from this detail, that we no longer employ bran at all for the whitening of maddered goods. It is also obvious, that we have infinitely reduced the heating operations, since formerly, a piece of goods, after the madding, received at least from three to six boils, whilst at the present day it gets one, or two at most, and it is an infinitely less time on the grass.

“I have often bleached maddered goods without giving them any boil, submitting them merely to immersions every twenty-four hours, and exposing them alternately on the field. But this has several inconveniences. In the first place, the goods are liable to have spots of a brick-red colour, which the workmen call *madder stains*; they proceed frequently from adulterated madders; an inconvenience felt only with the madders of Alsace. At other times, fat or oily matters, which are present in the goods, are the cause of them. These stains oblige us pretty often to subject the cloth to two boils, because the action of the acid, and the exposure on the grass, are insufficient.

“The goods, on coming out of the madder, are laid on the

field, because the large quantity of colouring matter deposited on their ground, destroys too great a quantity of the acid, and the colours are thus much impaired, which has led me to believe that they need the contact of air to be rendered fast, if it be permitted me to make use of this expression.

“The cloth, after the first exposure on the grass, is subjected to a boil with cow dung. This operation has the advantage of predisposing the cloth to become white, to heighten by its heat the colours fixed by the mordants, and to render them more durable under the action of the air, and of the solution of chloride of potash. I have diluted the liquor very much, because I do not then fear injury to any colour. I also pass through a colour that has a black ground, or its derivative hues, with as much confidence as those which have a mordant of alumina. The cloth, on coming out of these immersions, sometimes appears not to be sufficiently bleached, but they are wonderfully disposed to receive the action of the atmospheric oxygen. I have found several times, that on a piece of cloth being cut in two, when one-half of it had an immersion, and the other none, the former bleached more in two days on the field, than the latter in fifteen.

“When we are obliged to make the cloth undergo a second boil, it is given on its return from the grass, immediately after the first immersion in the liquor. By this second boil, we succeed in reducing entirely into a species of soap, and removing those spots of grease which I have mentioned above. This likewise dissolves the colouring matters which have begun to oxygenate.

“The cloths which come out of the weld, whether with a yellow ground or a white, are first exposed for four or five days on the grass, and are then, in like manner, subjected to an immersion in the same liquor. The ground of the goods does not appear at all bleached; but as I have already stated, they are disposed to receive the action of the oxygen, and at the end of two or three days' exposure on the grass, they are of a superb white. When these cloths return for the last time from the field, the yellow has a deep cast, which renders it somewhat dead.

“This probably depends on the action of the oxygen of the liquor, and of the atmosphere, which seems to have effected a commencement of combustion. Its vivacity is easily restored, by passing the cloths through a water very slightly acidulated

with muriatic acid ; but the water must be no sourer than weak lemonade. This operation has moreover the advantage of carrying off the last portions of the yellow which may have remained on the ground, or on the red ; and which, consequently, would dull the lustre of both. This little manipulation, which lasts, at farthest, five minutes, has also the advantage of rendering the olive colours more of a greenish cast, tints which the dyer has usually much difficulty to obtain.

“ I forgot to mention, that it is the strength of the colours which directs me as to the strength of the liquor. When the colours are powerful, I contrive it so that the chlorine may predominate in the liquor ; on the contrary, if the colours be weak, it is the alkali which ought to predominate. But if a saturated chlorate of potash were made, it would no longer have the property of bleaching. I suspected, that by passing cloths merely into an alkaline water, it would dispose them equally to whiten on the grass ; but experience has not realized this expectation.

“ I was a long while of obtaining complete success with the solution of chloride of potash, because I employed it in too strong a dose, and, of consequence, I injured the colours. But at present M. Oberkampf becomes every day more attached to this new method, which is infinitely less costly than the old one, and by which we obtain a more beautiful white, and far livelier colours.”

Widmer has, however, been obliged to abandon this process, because it required to be conducted by himself, and because the accidents, from inattention of workmen, rendered this method too uncertain and too expensive. We know not whether a like cause has made it be equally given up in the other manufactories, or if they have found out some modifications which render the process less uncertain ; but it should be retained for bleaching cloths in the texture of which there is linen or cotton dyed with some colour, which could not resist the too lively action of chlorine, or even exposure on the grass. (NOTE T.)

When we wish to deprive of colour a piece of cloth which has some defect of dyeing or design, or whose colours have been rendered dull by use, a ley should first be given to it, and then one immersion, which is commonly sufficient. It is now submitted to a second ley, and passed through water acidulated with sulphuric

acid. Without this last operation it would preserve a great part of its mordant, and could not, for this reason, receive a new impression or another design.

Chaptal made, at an early period, a happy application of the properties of chlorine to the bleaching of paper, and the restoration of engravings and books. We shall insert here the description which he gave of his processes.

"Blotting paper put into a solution of chlorine, becomes white in it, without being altered in its texture. The rags of coarse and bad cloth, made use of in paper mills to form this paper, are bleached by this solution, and then afford a paper of superior quality. I have whitened by this process a hundred-weight of paste intended to furnish blotting paper, and the increase of value in the product was estimated at 25 per cent, while the cost of the operation, rigorously calculated, did not raise the expense above 7 per cent.

"The property which this solution possesses, of bleaching paper, without affecting the texture, renders it valuable for repairing old books, and smoked engravings. Engravings injured to such a degree as to render the design difficult to be distinguished, have been repaired and refreshed in so astonishing a manner as to appear new. Old books, soiled with that yellow tint which time leaves on them, may be so restored as to make us think they had just issued from the press.

"Simple immersion in the chlorine, and a longer or shorter continuance in it, according to the strength of the liquor, are sufficient to bleach a print; but when a book is the object, other precautions are necessary. As it is requisite that the acid should moisten all the leaves, care must be taken to open the book well up, and to make its boards rest on the edge of the vessel, so that the paper alone dips into the liquor. Such leaves as are sticking together, must be adroitly separated, that they may be all equally impregnated. The liquor assumes a yellowish tint, the paper becomes white, and after two or three hours the book is withdrawn, in order to be plunged into pure water, which is to be renewed from time to time to carry off any remaining chlorine, along with its disagreeable smell.

"This process has succeeded with me pretty well. It was the first which I employed. But too frequently the colour of the leaves was variegated; sometimes several pages have not been at



all bleached; and I was forced to adopt a surer process. We begin by unstitching the books and reducing them to leaves. These leaves are set in squares contrived in a shallow leaden tub, with very thin plates, so that the leaves, laid flat, are separated from one another by hardly perceptible intervals. The solution is then poured gently in, making it fall on the sides of the tub; and to prevent the leaves from being deranged after the operation is finished, the liquid is drawn off by a stop-cock placed in the bottom of the tub. This liquid is replaced by fresh water, which washes the paper, and deprives it of the odour of the chlorine. It is now hung up to dry, smoothed, and bound. I have restored by this means several precious works, which were of no value from their bad condition. The leaves may be set also upright in the tub, a position which offers some advantages, as they are less readily torn. For this purpose I constructed a wooden frame, which I fixed down at the height which I thought suitable, conformably to the height of the leaves that I wished to bleach. This frame supported very thin slips of wood, leaving between them intervals of half a line. I placed two leaves in each of these intervals, and fastened them with two small wedges of wood, which I pushed between the slips so as to press the leaves against them. I give the more preference to this process, because, when the operation is done, I lift out the frame with the leaves, and plunge the whole into fresh water. By this operation, not only books are restored, but the paper receives a degree of whiteness which it never had. This acid has also the advantage of effacing spots of ink, which frequently depreciate books and prints. This liquor does not attack the stains of grease or oil; but it has been long known, that a weak solution of potash (caustic alkali) is a sure means of removing these marks.

“When I have had to repair engravings in such bad condition that they exhibited merely fragments pasted down on paper, I was afraid of spoiling these fragments in the liquor, from the loosening of the paste. In this case, I took the precaution of enclosing the print in a large cylindrical jar, which I inverted over a glass, into which I put the proper mixture for disengaging chlorine gas. This aeriform substance filled the interior of the jar, and acted on the print, consuming the filth, destroying the spots of ink, while the fragments remained glued, and thus preserved their relative position.”

Loyssel has prosecuted particularly the application of chlorine to the bleaching of the paste of paper, because he was charged, as member of the committee of assignats and coins, to inspect this process, which was used for the assignat paper. We shall present a summary of the observations which he published.\*

By the ordinary processes, only a small portion of the rag can furnish fine white paper; all the rest being appropriated to papers of inferior quality.

The bleaching of the paste of paper, even when derived from the most ordinary rags, can give it the quality of that of the finest rags.

The tenacity of the paper depends on that of the fibres of which it is fabricated. The rags of new cloth and cordage afford a tougher paper than old rags. In the first rank are put rags of fine new webs, either green, or bleached by the chlorine; after these come cordage and old rags.

The paper intended for bank-notes, or bills of commerce and service, should be tough, to render it less apt to be torn than its thinness would otherwise occasion. For this, it is right to employ in whole, or in a great measure, materials of the first class.

The processes prescribed for the bleaching of threads and cloths must be employed here; that is to say, the substance must be subjected to *lixivia* and immersions in the chlorine liquor, when it is green (unbleached); but in operating upon rags, it is sufficient to give them an immersion, and to pass them afterwards into acidulated water.

An inconvenience has been experienced in operating upon the paste of paper. It appeared very white, and yet it furnished an unequal paper. It was because this paste subsided, so that the leys and the liquors could hardly penetrate it. This inconvenience was remedied by taking the matter in a medium state, between that of a paste and of rags. This was secured by tearing it asunder, under a first cylinder, thus destroying the texture of the rags, and separating the fibres that composed the thread.

When a very tough paper is wanted, the green rags must be submitted to the successive operations of bleaching. But when whiteness is the principal object, the cost of the operation may be considerably diminished, by leaving the rags for some time

\* *Annales de chimie*, tom. xxxix.

in the fermenting tub, and washing them with care. After this, one lixivium, two chlorine solutions, and acidulated water, will be sufficient.

In this operation, the combination of chlorine and potash, dissolved in twenty times its weight of water, has been employed. Undoubtedly, with a suitable apparatus, there might be used without inconvenience simple solution of chlorine, or this mingled with chalk.

Notwithstanding the increase of expense caused by this addition of alkali, Loysel shows, that the value added to the paper by the process affords a considerable profit.

In treating of hemp and flax, we have described the processes by which it has been attempted to give them the appearance of cotton. Chlorine may be beneficially employed for this purpose.

Pajot des Charmes seems to have been the first who made this application. We shall recite the passage where he points it out.\*

After having announced that the loose fibres bleach very quickly, that is to say, at one or two immersions less than average yarns, he adds: "It is to be remarked, that the tow of flax or hemp proceeding from the fibres thus bleached, or bleached separately, cut, if it be too long, and then carded, singularly resembles the cotton of Siam, which is known to be the shortest and the most common of the cottons of commerce. When it is well carded, their difference cannot be discerned; nor is it possible to distinguish between them in spinning. I took occasion to make some of it be woven at the end of a web: it would have been taken for real cotton. I took occasion, in like manner, to employ some of it for candle-wicks, without any perceptible difference being found by the quantity of light or the brightness. It would be very interesting, without doubt, to know all the benefits which could be derived from this application of chlorine to the arts of life."

Some time thereafter, but without knowing what has been now detailed, a description of operations made in the laboratory of the Polytechnic School, to accomplish the above object, was published in its Journal. But Giobert has given us more extended and more exact observations, capable of directing this new branch of art, which may probably acquire some importance.†

\* *L'art de blanchiment*, page 106.

† *Bibliot. ital.* vol. ii.

"The process which I have followed," says he, "is in general the same as what Berthollet has just proposed, but with this difference, that in the trials made at the Polytechnic School, long fibres cut in fragments about  $2\frac{1}{2}$  inches in length were employed; whereas, in all my attempts, and in my operations on the large scale, I employed merely hemp tow of the worst quality, at three sous the pound.

"The process which Berthollet describes is the same, and consists of the following operations:—

"The fibres are covered with water, and left in it for three or four days; after which they are boiled in simple water.

"2. They are treated with a ley, and then passed into the chlorine; operations which should be repeated alternately four times.

"3. The fibres are now transferred into a bath of water, charged with one-hundredth of sulphuric acid, and left in it for half an hour.

"4. The fibres, when taken out of this bath, are washed very carefully, and plunged in soap water. They are then stretched out, without wringing, on hurdles, and left to dry.

"On this process Berthollet has remarked, 1. That it requires only from five to six hours when small quantities are operated on; 2. That the loose fibres thus prepared, were capable of being spun into very fine yarn of sufficient strength, although the filaments had been cut very short in his trials; 3. That the leys should not be too strong, but that they should be boiling hot; 4. That whether the finest flax or the coarsest hemp tow be employed, we obtain filaments equal in their fineness and whiteness; finally, he adds, that he believes by preventing too strong desiccation, the last immersion in soap water might be suppressed.

"The different observations which we are going to make on this process, are the result of operations on a large scale, which have brought into the market *cottony* cloth, and *bales* of this hemp-cotton, which were not distinguishable from ordinary cotton. From these results, various ameliorations have suggested themselves. We shall follow in our operations the same order as ought to be pursued in the practice of the above process.

"1. *Preliminary maceration of the fibres, (filasse.)*

"This operation is not absolutely necessary, and it may be supplied by a good ley. But a previous maceration is more eco-

nomical. Instead of pure water, old ley should be used in preference; but if there be none of this, plants, especially mucilaginous ones, boiled in water with the addition of a little potash, afford a better solvent. The steeping may also be continued longer, even for five or six days, without risk in the hottest season, along with the employment of alkalies that seem to favour the putrid fermentation. In spring, autumn, and winter, it may be prolonged with advantage from seven to nine days. By this longer maceration, the fibres become finer, that is to say, the filaments come asunder, and the operations to which they are subjected in the sequel have a greater effect.

“ When the fibres are well steeped, it is absolutely useless to wash them with hot water, which only augments the cost. Cold water is sufficient; but it must be in a stream, treading the fibres with the feet till the water issues very clear.

“ 2. *Of the leys and immersions in solution of chlorine.*

“ The leys might be dispensed with, by abandoning the fibres to fermentation, in the manner above stated, after having passed them through the chlorine; but this practice is too tedious. Nothing however occasions more inconvenience here than the *lixiviation*. Every filament of hemp or flax which has been *lixiviated* thence derives stiffness, especially in its extremities, which are to be joined continuously in the formation of yarn. Hence its spinning becomes difficult, disagreeable, and unequal. The spinster loses patience; while the ends of the fibres do not twist well together, their adhesion is imperfect, and by sliding on each other, when the thread is slightly pulled, render it feebly tenacious. This may be regarded as a general fact. Yet leys can hardly be dispensed with in a great manufacturing establishment of hemp-cotton. For this reason, we must try to remedy these inconveniences, which cannot be economically avoided. We shall point out by and by two methods which succeed pretty well. As to the leys, they ought not to be strong, as Berthollet rightly says; but they should be very caustic, carefully preventing an excess of lime or of lime-water in the liquor; for, in this case, the fibres are too much weakened on one hand, and grow stiff on the other. A ley is not too caustic, when on evaporating a portion of the liquor, it is not disturbed, nor lets fall lime. The ley-boil ought not to exceed three hours; but after this the greatest part of the liquor must be drawn off, and the fibres

must be allowed to cool in a heap in the tub before washing them. It is useful to place on the cloth which covers the fibres large compressing weights. This repose of the fibres with little liquor, has a more decided effect than the lixiviation; and the larger the quantity operated upon, the better does it answer.

"It is useful to arrange the apparatus, so that the fibres can be thereafter washed by a stream of water in the very tub in which the lixiviation has taken place; and it is in this same tub that it is afterwards subjected to the chlorine, which ought to be very weak.

"3. *Bath of sulphuric acid.*

"An acid bath is indispensable to give a shining whiteness to the fibres. But these when bleached contain lime, which, forming an insoluble salt with sulphuric acid, causes this to be ill adapted for the purpose. The resulting sulphate of lime adheres to the fibres, making them rigid; nor is it possible to carry it entirely away by washing. I have found, that by substituting muriatic acid for the sulphuric, the fibres have more pliancy. Muriatic acid has a somewhat higher price in commerce; but by making it within the manufactory, the expense incurred by this substitution is not very considerable, and it ought to be preferred.

"4. *Soaping.*

"The last operation is the soaping. This is indispensable; nor ought any person to imagine he can do without it, for it is only by the soaping that we succeed in thoroughly separating the filaments. Besides, it is only by the soaping that we begin to correct the rigidity which the ley gave to the fibres, and to give them the pliancy of ordinary cotton. But to attain this end, we must proceed in a different manner from that described by Berthollet.

"The fibres, on coming out of the preceding bath of muriatic acid, instead of being washed with much care, as is stated in Berthollet's process, ought not to be washed at all. They should be plunged, while still wet with the acid liquor, into the hot soap-water, without fearing in the least the action of the acid. The soap is decomposed by the acid, the resulting muriate of soda is carried off by successive washings, and the oil of the soap being absorbed by the fibres, gives them pliancy and softness. The filaments remain more delicate, and the successive

operations of carding and spinning become consequently easier. This is the first of the two methods which we announced for removing from the fibres the stiffness which the alkalies of the lixivium gave them.

*"5. To give pliancy to hemp-cotton.*

"Notwithstanding the preceding processes, the cotton has not yet got all the pliancy which is required. This will be completely given by the following operation. The dried fibres are formed into large bales, and kept well packed up in a somewhat damp place for two or three months. A species of fermentation is by this means excited in the fibres, which gives them the desired fineness.

*"6. To give the appearances of ordinary cotton to hemp-cotton.*

"The cotton procured from hemp by the preceding operations, whatever care may have been bestowed, is always different from ordinary cotton, and it is easy to distinguish it. The fibres preserve a peculiar glitter very different from the dead white of cotton. This lustre is sufficiently agreeable, and may possibly be sought after for several objects of manufacture; but it is not a property of cotton, and must therefore be regarded as a defect in our attempts to imitate ordinary cotton. I have discovered only one method of remedying it, which consists in mixing by the cards from 10 to 15 per cent. of ordinary cotton with that of hemp. The cotton yarn made by this means is no longer distinguishable from ordinary cotton yarn."

## SECTION IV.

### OF DYEING OPERATIONS IN GENERAL.

#### CHAPTER I.

##### *Of Dyehouses and the Manipulations of the Art of Dyeing.*

IF it may be regarded as a general principle, that processes performed in a great manufactory are more advantageous than those which are insulated, (*isolés*), since from the subdivision of labour each workman, occupied with a single object, acquires celerity and perfection in his employment, and since every thing being concatenated, each portion of the work is carried forward without loss of time; this principle should be applied to dyeing for a peculiar reason, because the residuum of one process can frequently serve for another. A bath which is found to be too much exhausted for one colour, or even for what is called the *suites* (gradations) of a colour, may either give a ground (*footing*) to other dye-stuffs, or form a new bath, by mixing other ingredients with it. Gall-nuts which have been employed for galling silk, may still be useful for other operations on wool and cotton. A great number of similar examples might be adduced.

By such considerations, it would be easy to prove how adverse to the advances of the art were that division into the *great and little dye*, that classification of silk, wool, and linen dyers, and those regulations which prohibited a dyer of one class to keep by him the ingredients assigned to another class. On the contrary, it seems proper to encourage large undertakings in dyeing; and those who are to direct them ought to lay down a plan of the operations, so that there may be a relation between them all, and that there may be no waste of ingredients, time, fuel, or manual exertion. This arrangement should be made subservient to the probable demands of commerce.



A dye-house ought to be spacious, well lighted, and as near as possible to a stream of water. It should be floored with lime and cement; it should be provided with ready outlets for the water and the spent dye-baths; and the whole so ordered as to secure the utmost cleanliness.

The boilers, whose arrangement and size depend on the operations for which they are intended, should be made of copper or brass; except for dyeing scarlet, for which it is better to employ boilers of tin, as well as for other delicate colours, where a solution of tin is made use of. Brass is less liable to be attacked by saline substances, and to stain the goods, than copper. We shall see, however, that in many cases vessels of wood may be substituted for metal boilers. It is of consequence to cleanse the boilers well after every operation; and such as are of great capacity ought to have in their bottom a copper pipe, with a stopcock at its outer end, which is opened when the baths are to be emptied.

Above each boiler, holes are pierced in the chimney-piece or wall, for resting the ends of poles, which serve to sustain the hanks of wool or silk while draining, or stuffs of which only small portions are to be dyed. Thus also the bath liquor falls back into the boiler.

For piece goods, a winch or reel is employed, the two ends of which rest in two forks of iron, placed, at pleasure, in holes bored in the curb that supports the edges of the coppers.

Several silk and cotton dyes, for which ebullition ought not to be employed, are performed in long vessels of copper or wood, called troughs or backs, (*barques ou baquets*.)

As the most part of colours applied on silk are very delicate, they require to be speedily dried to prevent their changing. For this purpose a drying room is provided, which is heated by means of a stove. The silk is stretched on a moveable pole called a shaker, (*branloire*), which is hung up and agitated to accelerate the desiccation. A drying room is also used for cotton cloths which have been impregnated with a mordant.

Long details must be entered into, were we to describe every thing which constitutes a dye-house. Inspection will instruct much more speedily and exactly than a minute description of these objects could do. The distribution of a dye-house ought also to be subservient to the operations for which it is destined.

It should be so regulated, that these operations may follow one another with the most advantage.

But it is desirable for the advancement of the art, as well as that of the science itself, that a small place may be reserved, in which the apparatus necessary for the common experiments of chemistry and the trial of dyes may be collected.

The manipulations of dyeing are neither difficult nor complex. Their object is, to impregnate the substance which we wish to dye with the colouring particles held in solution in a bath; to make the agency of the air co-operate in the fixation of the colouring particles, or in giving them lustre; and to discharge with care such as have not been fixed in the dyed stuff. We shall content ourselves with giving an account of the most common manipulations, and of the denominations.

When one or more pieces of goods are to be dyed, the winch (reel) is employed as above described. One end of the cloth is wrapped round this reel, which being turned quickly, carries round the whole piece in succession. The winch is next turned in the opposite direction, in order that the part of the web which was first plunged the former time, may be last at the second immersion, whereby the dyeing is rendered as equable as possible. If the piece of goods be long enough, or if several are to be dyed of the same colour, their two extremities are stitched together, the winch is passed within, and then set on its forks.

When a solution of iron is employed, especially to give different shades to cotton goods, which are, for example, to be afterwards passed through madder, we must prevent with great care the progressive and unequal oxydation of the metal, according to the directions of Chaptal on this subject,\* which we shall take occasion to recite.

If wool in the fleece is to be dyed, there is set over the boiler a very broad kind of ladder, (called by English dyers a *scraw* or *scray*,) the bars of which are very close together. On this the wool is laid to be drained and aired, as well as during the changing of the bath.

When the wool is in skeins, a rod is passed through each of them, and the manipulation is the same as for silk and thread. This manipulation consists in turning round in the bath the

\* *Memoires de l'institut*. tom. iii.

hanks of silk, and the skeins of thread or woollen yarn on the rods. This is called *liser*, (shaking over,) and to the rod the name *lisoer* (skein stick) is given.

After silks and yarns have been dyed, it is necessary to wring them, in order to squeeze out the excess of the colouring particles. This operation is performed on a cylindrical piece of wood, which is fixed at one end in a wall or to a post. It is called *espart*. When this operation is repeated several times in succession, in order to dry and give lustre, it is called *chevieller*, (wringing by the jack and pin.)

When a certain quantity of ingredients is added to a bath, it is said that a *brevet* is given it; and it is pallied (*on le pallie*) by stirring it about and mixing it with a rake.

Sometimes a first colour is given in order to apply another one above it, thus forming a compound colour. This is what is called *giving a ground*, (*donner un pied*.)

*Disbroder* (*rinse*) is to wash silk from its dye, or its soap water, in a small quantity of water, to which the name of *disbrodure* (*rinsing*) is given.

When a stuff must be passed several times through the same bath, the name *passe* (*dip*) is given to each particular operation.

A colour is *rosed*, when the yellow tone of a red colour is changed into a shade which borders more on the crimson, or on the colour of roses; and a colour of a red-yellow is *veered*, (*virée*), when it is made to turn to a more decided red.

Although the manipulations of dyeing may not be very various, and may appear very simple, they require peculiar care, as well as a skilful eye, to judge of the qualities of the bath, to raise and support the heat at the degree suited to each operation, to remove all the circumstances which might produce inequality in the colour, to judge with precision of the shades as they come out of the bath, to match those which serve for patterns, and to establish the desired relation between a succession of hues.

## CHAPTER II.

*Of Fuel.*

As fuel is one of the chief articles of expense in dyeing, it is of great consequence to diminish its consumption as much as possible, and to select the kind which may afford the desired effect with the least cost. It is proper, therefore, to be acquainted with the philosophical principles of the production of heat by combustion, the theory of which we owe chiefly to Lavoisier, as well as with the laws of its communication, in order to be able to guide ourselves afterwards in their application to the various circumstances that may occur.

When a body is burned, none of its ponderable principles are destroyed. They previously formed a mere combination with each other, and they are separated at the high temperature to which they are exposed; thus forming other combinations with the oxygen with which they come into contact. Such of these principles as cannot combine with it, that is to say, earth, certain salts, and metallic ingredients, constitute the ashes.

The combinations formed, when the reciprocal action of the oxygen gas and of the inflammable principles present in the combustible becomes complete, are carbonic acid and water. The proportion of these products varies, according to that of the carbonaceous particles, and that of the hydrogen or base of inflammable air which exists in the combustible. Let us take common charcoal for an example:—

If 100 parts of charcoal be burned in a glass bell, whose orifice is plunged under mercury, there is found, after the combustion, a weight of carbonic acid, equal to that of the charcoal burned, and of the oxygen, which has now lost its properties. This acid so formed, is composed, in 100 parts, of about 72 of oxygen, and 28 of carbon. A little water is however generated, which is taken up by the carbonic acid, or remains in the liquid state. The unknown quantity of water prevents us from regarding the determination now given as rigidly exact.

If alcohol or spirit of wine be burned, the result is different. A weight of water is obtained exceeding that of the alcohol, because the combustible principle of alcohol is chiefly hydrogen,

which forms water by combining with oxygen. Oil also affords much water, for the same reason. Charcoal and alcohol, or rather ether, may be regarded as the two extremes, of which one yields most carbonic acid, and the other most water; and the other combustibles may be viewed as mean terms, which approach more or less to one of the two extremes, according to their composition.

While the hydrogen and the carbon combine with the oxygen, which forms a little less than the fourth part of the atmospheric air, the caloric or principle of heat, which was combined with the oxygen gas, giving it the elastic state, is in a great measure disengaged. A portion of it is also probably disengaged from the carbon, and especially from the hydrogen, but as the heat produced when oxygen passes from one combination into another, appears nearly proportional to the quantity retained, we depart very little from the truth, in ascribing to it the whole heat disengaged in combustion. Hence the heat produced in combustion must be regarded as proportional to the quantity of water and carbonic acid formed. We must however remark, that the same quantity of oxygen which enters into combination with hydrogen to form water, gives more heat than when it produces carbonic acid with carbon. Hence combustibles which contain much hydrogen, such as the oils, the resins, and pit coal, produce in equal weight, and in circumstances equally favourable, more effect than those which owe their inflammability to carbon.

If the proportion of oxygen gas which combines be insufficient, (for saturation,) water and carbonic acid are not the sole products. A gaseous substance is formed, which may be regarded as intermediate, being convertible into water and carbonic acid, by means of a new proportion of oxygen. It has been named *oxycarburetted hydrogen*, in order to denote its composition.\*

Oxycarburetted hydrogen gas produces the blue flame over furnaces, when its temperature is great enough to burn on passing into the atmosphere, where it finds the oxygen which was deficient in the furnace.

The conditions necessary to obtain the greatest effect of combustion may be established on the foregoing considerations: 1. The quantity of oxygen ought to be sufficiently great for the

\* Statique chim. tom. ii.

whole charcoal and hydrogen to enter into complete combination, without producing oxycarburetted hydrogen gas, and without the combustibles escaping under the form of soot or smoke.

2. On the other hand, too great a proportion of air must be avoided, for whatever is useless to the combustion, by abstracting the heat disengaged from the fuel entering into combination, would obstruct the elevation of temperature which is the object of the combination.

3. The current should be rapid, that the heat may become intense, and the temperature be sufficiently elevated for every thing combustible to undergo the oxygenous combination.

In order to obtain the greatest effect of a combustible, none of its particles capable of combining with oxygen should escape the operation; there should be neither soot nor smoke; a result obtained chiefly by the just proportion between the lower opening of a furnace, its grate and chimney.

The current of air which maintains combustion should be easy; but if the chimney is too large, the carbonic acid formed is carried off with difficulty; it remains too long in contact with the combustible body, thereby opposing its combustion, while an interior circulation is established, which brings back the cold air towards the boiler, and pushes down the smoke. If the chimney is not high enough, a portion of the inflammable gas escapes without burning, as well as the carbonaceous particles that form the soot; whence the effect of the combustible is diminished. A higher column of air, rarefied, and rendered lighter by heat, and next its condensation, as well as that of the steam and carbonic acid, towards the top of the chimney, would have contributed to establish a more rapid aerial current. These effects are peculiarly observed in reverberatory furnaces, in which it is easy to verify the benefit of a chimney whose opening is in due proportion to the size of the furnace, and whose activity is increased by adding to the upper orifice a certain extent of pipe. But too lofty a chimney is another inconvenience to be avoided; because the combustible parts which rise have time to cool below the degree at which their combustion takes place, forming merely a mass, which, with the carbonic acid, opposes the circulation of air.

When a furnace is intended for a boiler or a series of boilers, it must be so managed that the combustion is completely exe-

cuted in front of the space in which the heat should be concentrated. In order to obtain this effect, it is proper that the grate (hearth) in which the combustion takes place be in front of the boiler, as Curadau recommends,\* to whom we owe several interesting observations on the regulation of furnaces. Since the current of air is greatly more rapid when the furnace has a high temperature, it is proper to diminish its column by means of a register (damper) placed in the chimney. This register serves likewise to intercept the current when the combustion is finished, and when we wish to turn the remaining heat to account by preventing it from being hurried off by the air.

The form of boilers is not unimportant towards obtaining the greatest effect of fuel with the least cost and loss of time. It should be subordinate, however, to the kind of operation that is intended. We shall restrict ourselves to a few observations on this subject.

The boilers should present the utmost possible surface to the fire, and the heat should be applied to the greater part of their outer surface by making the flame circulate round them. Consequently, when they are intended for evaporation, distillation, or the heating of liquids, as leys for example, their width should be greater than their height. Chaptal recommends, moreover,† to construct them so that the bottom shall be convex within. By this construction, the insoluble parts thrown off upon the sides obstruct less the communication of the heat, while the copper at the bottom is longer preserved.

It is not enough to pay attention to the combustion, but the resulting heat must be distributed also, so as to produce most advantageously the desired effects.

There are bodies which afford a ready passage to heat; such, in particular, are metallic substances. There are others, on the contrary, which conduct it slowly and with difficulty; such are glass, pottery, bricks, woollen tissues, ashes, and especially charcoal. The latter substances ought therefore to be made use of, either directly or as envelopes, when it is desired to maintain the temperature; but metallic substances, when the heat is to be diffused. The colours of the surfaces which disseminate or receive heat, may also possess an influence, according to the recent

\* *Annal. de chimie*, tom. xlv.

† *Elemens de chimie*, tom. i.

ingenious observations of Count Rumford ; but we are not yet acquainted with their applications to the arts.

When the object is to form a solution, attention ought to be paid to the effect that specific gravity may produce on the solution, or on the communication of the heat.

Every chemical combination, and that of caloric, which follows its laws, are more speedily effected the more distant the point of saturation. Hence, when a salt is dissolved at the bottom of a liquid, which thus acquires a greater specific gravity by its saturation, the successive layers of liquid are kept in their respective position, and the most saturated remain at the bottom. There is but a slight difference in saturation between each of the layers, and thus the equilibrium of the whole is long of being acquired. But if the salt is placed at the surface, the portion of the liquid which becomes saturated falls to the bottom in consequence of the specific gravity which it has acquired. A current is established which continually brings the least saturated liquid in contact with the salt, whence the solution is more quickly made, even without employing manual agitation, which also acts by approximating the less saturated portions to those which are completely so.

On these grounds we have recommended, after Welter, to operate at the surface of the water the solution of potash intended for leys. If a gaseous substance is to be dissolved, the solution should, on the contrary, be effected in the lower portion, in order to keep at a distance, by a less specific gravity, the liquid which may be already saturated.

When water is converted into vapour by ebullition, it contains a great deal of caloric in a latent state, which it gives up when restored to the liquid condition. It results from the experiments of the celebrated Watt, that this quantity would be sufficient to raise the thermometer of Fahrenheit 900°, or the centigrade thermometer 500° ; whence it follows, that one part of steam at the temperature of ebullition can raise, by losing itself the vaporous state, five parts of water from the temperature of zero to the boiling point.

We thus perceive what advantages might be derived from the steam that issues from boilers ; but the requisite manipulations would seldom permit us to take the full benefit of it.

The celebrated Rumford, to whom we owe a great many



ingenious observations on heat, its distribution, and the economical use of fuel, has pointed out modes of employing the vapour of water for the communication of heat, which may be peculiarly advantageous in the art of dyeing. We shall give some account of them.

The purpose of the apparatus is to generate steam, to be carried into a vessel filled with any liquor which we may wish to heat by its agency. A boiler must therefore be procured for keeping up the ebullition of water. It ought to be spacious enough to form a sufficient quantity of vapour; and agreeably to what has been described, it ought to have greater length than height, and be so placed in the furnace as that most part of the circumference shall be exposed to the current of flame.

This boiler must give origin to a large pipe, which serves as a reservoir of steam. From this reservoir the conductor tubes branch out, which are to transmit the vapour into the receivers to be heated. These tubes should have a slight inclination, that whatever vapour has resumed the liquid state may flow back into the boiler. Into the end of each a vertical tube enters, which carries the steam into the lower part of the receiver, and which may be placed even in the inside of the receiver, or on its outside surface. Above the level of the liquid the latter tube should have an accurate stopcock, to prevent the liquid from rushing back into the boiler when its steam is condensed by cold, or has lost some of its elastic force. To prevent the accidents, however, which might be occasioned, either by negligence in shutting the stopcock, or, on the other hand, from so rapid a formation of steam as might burst the apparatus, the boiler ought to be provided with two valves, one intended to permit the introduction of air when a vacuum is formed interiorly, the other to give an outlet to the steam when its force becomes too considerable.

To supply the steam-boiler with water, a reservoir is needed, which communicates with it by means of a tube. This ought to have a stopcock opening by means of a floater, when the water of the boiler is diminished to a certain point. This tube should be more or less elevated, according to the degree of temperature which the steam is to possess; for without sufficient pressure, the vapour of water could not raise the water which condenses it to the degree of ebullition. This circumstance

obliges us to give the boiler sufficient thickness to support the expansive action of the steam at a temperature above the boiling point. The water contained in the reservoir may be prepared to produce its effect, by previous heating through the prolongation and distribution of the chimney of the furnace.

The whole outside of the apparatus must be preserved from the loss of heat, by surrounding it with non-conducting substances. The author recommends to apply, by means of paste, to the surface of the tubes, two or three coats of paper; and still better, hemp wrapped round in the direction of its filaments. He has made curious experiments on the power which this envelope gives. They are next surrounded with a wooden case filled with charcoal dust, or pounded bricks.

In this way dye-baths may be heated, substituting wood for metals, and heating several by means of a single furnace, which may be at the same time portable. Different degrees of heat are given, according to the dimensions of the tubes which conduct the vapour into each bath; and an uniform temperature is obtained. Lastly, the same method may be applied to the construction of drying rooms and stoves, the condensed water being reconducted into the boiler.

This method, which may be varied and multiplied in its applications, deserves peculiar attention, since English industry has already turned it to several purposes. (NOTE U.)

Having thus given an idea of the phenomena of combustion, and pointed out the means of profiting by the heat, it remains to consider the different kinds of fuel, in reference to their peculiar advantages.

To compare the effect of different combustibles, the process described by Lavoisier may be employed.\* It consists in burning each species of combustible in the same furnace, over which a boiler is placed. Into this boiler an equal quantity of boiling water is poured, and what has been evaporated is replaced by letting in an equal weight of water at each operation. The quantities of fuel required to evaporate the same quantity of water are afterwards compared. It is obvious, that the qualities of the combustibles are proportional to the quantities necessary to produce the same effect. We have to compare, then, merely

\* Mem. de l'acad. 1781.

the quantities of each combustible employed in the evaporation, with its respective prices, in order to determine what are the most advantageous, and ought to be preferred. For this calculation, the weight or volume of each combustible may be made use of indifferently, provided the price of the measure be known.

Instead of evaporating the same quantity of water, the desired result may be equally attained, by burning either the same weight or the same measure of each kind of fuel, and comparing thereafter the quantities of water evaporated.

As the bulks and weights of fuel should be compared with the price, and as this price varies considerably in each country, nothing of an absolute nature can be established concerning the combustibles whose employment is the most profitable. In one place it will be pit-coal; in another, it will be wood or turf; the ratio of the prices may vary even in a short time, either by opening a canal, by working a mine of pit-coal, or by the destruction of a forest. Several operators retain a prejudice against the use of pit-coal; but it is enough to observe, that it is at present employed in so great a number of dye-houses, without any inconvenience being experienced, that there can be no doubt of its answering as a substitute for other fuel; but as in equal weight it yields much more heat, a little practice is required in its management.

Pit-coal requires in the furnaces a construction somewhat different from that of the furnaces in which wood is used. As it kindles with difficulty, it must be burned on a grate, which affords passage to a current of air. Its qualities are moreover very variable; and the kind useful for one purpose is not fit for another. Even should experience prove, that there is no advantage in our country in preferring pit-coal to wood, the use of it should be begun; because it is very probable, that the price of wood will progressively increase, while, on the contrary, that of pit-coal will fall, because its mining will be promoted by being made with more intelligence than it has hitherto been in France, and because it is to be hoped that canals for facilitating its carriage will be multiplied.

Pit-coal is reduced into a true charcoal, by an operation analogous to that by which wood is carbonized; an operation to which the name of *dessoufrage* (cokeing) is given. This charred coal affords a real advantage in the great furnaces, which serve to

smelt ores of iron, because pit-coal swells and agglutinates when it is highly heated, thereby choking the furnaces; inconveniences which it no longer possesses after being coked. But for other uses, it is preferable in its natural state; because all the bituminous oil burned off when it is reduced into charcoal is wasted, without producing any effect; and this operation requires labour, which must be paid for.

Turf (peat) is also reduced to charcoal; but this operation presents a difficulty not easily overcome. When the recent charcoal of turf is exposed to the air, it takes fire of itself, like a pyrophorous; an inconvenience which has, however, been eventually obviated.

What has been said of pit-coal is applicable to turf. When it can be employed in its natural state, it is more profitable to do so than to incur the necessary expense of converting it into charcoal, with the loss at the same time of the whole portion which is consumed in this operation, and which could have served to produce heat.

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### CHAPTER III.

#### *Of the Means of ascertaining the Goodness of a Colour, (Dye.)*

As colours differ greatly from one another, in their manner of resisting the action of air, light, and other agents to which they may be exposed; and as in this circumstance an important quality consists, of which the eye is no competent judge, methods have been sought after for verifying their goodness by easy and ready tests.

The purpose of these tests was to condemn the dyes which could not resist them. It is truly important to protect commerce from the frauds which may impair the confidence of which it stands in need; and its interests would be promoted were we able to assign the standard of manufactured productions like that of gold and silver. But is it possible to find means sufficiently certain, and at the same time expeditious, capable of determining the permanency of a colour as well as its lustre, and the other qualities which it is desired to possess? Were these means found out, could they be applied with equal success to the

processes which an active industry discovers and introduces every day?

Much importance has been assigned to those tests formerly called *debouillis*, at a time when the processes of the arts were subjected to regulations which sometimes directly counteracted their advancement. By these, the workman in the fugitive *dye* was punishable for employing certain ingredients capable of giving fast colours.

These shackles were perhaps necessary to the establishment and early progress of industry; but at the present day, they are irreconcilable with its interests. With regard to goods which are to be exported, it is possibly wrong to depend upon such indications of manufactures as are exacted from the *chefs des pièces*, (inspectors of dyes.) It is well known how much our commerce has lost in the Levant by fraudulent fabrications and dyes, under known appellations.

We shall not examine this question; but we shall recapitulate what experience has taught concerning the methods which may be employed, among which a dyer may select some profitable even for his own use. We are peculiarly induced to do this, because the tests at first prescribed have been rectified by the experiments of Dufay, a philosopher possessed of much sagacity. We shall now, before transcribing the instruction founded on his trials, present the history which Hellot has given of them, with his judicious reflections.

“Since it cannot be exactly ascertained, either by informations taken from different dyers, or by the perusal of ancient regulations, what are the precise characteristics of the colours of the good dye, (fast,) or those of the small dye, (fugitive,) it became necessary, in order to acquire this knowledge, to take the longest, the most difficult, but, at the same time, the most secure, or to speak more properly, the only method on which it was possible to depend with certainty. The late M. Dufay, of the Royal Academy of Sciences, whom the government appointed to labour towards the perfection of this art, caused woollens to be dyed, under his eye, of all colours, and with all the ingredients which are used in dyeing, both in the *great* and *little dye*, (in fast and fugitive colours.) He even brought from different provinces articles not employed at Paris. Lastly, he collected most of the materials which he suspected to be made use of in

dyeing, and he tried a very great number of them, without attending to the prejudices of dyers relative to their good or bad qualities.

“He began his trials on woollen yarns, but he found in the sequel, that pieces of white cloth were more convenient for the experiments which he had the intention of making.

“In order to ascertain, among the different colours, those which were solid, and those which were not so, and consequently distinguish the fast from the fugitive dyes, he exposed to the sun and the air during twelve days, patterns dyed by himself of all those colours with whose composition he was acquainted. This period seemed sufficient to prove them; for good colours are either not at all damaged, or very little, while the spurious are in a great measure effaced. Hence, after twelve days' exposure to the sun in summer, and to the moisture of the air during the night, no doubt could remain about the class to which each colour ought to be assigned, when it was tried in this manner.

“Nevertheless, one difficulty still remained; for, not having exposed all these colours to the air precisely at the same time, or in the same season, some of them must have had more sun than others, and must, of consequence, have lost more in the same space of twelve days, than those which had been exposed in gloomy weather, or when the days were shorter. But he obviated this inconvenience, so as to leave no more difficulty or doubt of the correctness of the test; for he selected one of the worst colours, that is to say, one of those on which the sun had taken the most sensible effect during the space of twelve days. This colour served him as a comparison piece for the whole course of his experiments, and every time that he exposed the patterns to the air, he annexed to them a piece of this same stuff. It was now no longer the number of days to which he had respect, but the colour which his comparison specimen assumed, and he kept this exposed till it had lost as much as the piece which had been exposed during twelve days of summer. As he always noted the day on which he exposed his specimens, he had occasion to observe, that in winter it was sufficient to leave them in the open air four or five days longer, for them to lose as much colour as they had done in summer. By pursuing this method, no scruples remained in his mind about the accuracy of his experiments.

“In this proof, by exposure to air and the rays of the sun,

he had still another object, it was to find the *debouillis* suitable to each colour. The term *debouilli* or *debout*, denotes the test which is applied in order to learn if a stuff has a fast dye or otherwise. A pattern is boiled with alum, tartar, soap, vinegar, lemon-juice, &c.; and from the effect of these drugs on the colour, its quality may be judged of. The *debouillis* practised up to the year 1733 were so insufficient, that they could not serve to M. Dufay as indications for finding out surer ones. Indeed, some good colours were thus carried off, while the bad ones were very little damaged. Hence he was obliged to fix on several tests, each of which serves for a great number of colours. The following is in a few words the path which he pursued in order to find them.

“ After having observed the effect of the air on each colour, whether good or bad, he tried on the same stuff different species of *debouillis*, and he kept by that which had the same effect on this colour as the air had produced. Noting afterwards the weight of the drugs, the quantity of water, the duration of the trial, he was sure to produce on that colour an effect equal to what the air ought to make on it, supposing that it had been dyed in the same manner as his own had been, viz. according to the method either of the fast or fancy dyers. Making thus a survey of all the colours, and of all the ingredients used in dyeing, he discovered a method, which may be regarded as accurate, of knowing the good or bad quality of each colour, making by the *debouilli* a kind of analysis of its composition. We cannot without injustice fail to acknowledge, that the means which led M. Dufay to the discovery of these *debouillis* or tests of colours, are very ingeniously imagined; because the trial by the air and sun cannot be put in practice in cases where it must be decided on the spot, whether a stuff, exposed to sale, in a fair or elsewhere, is of good dye, should its price correspond to this quality.

“ The *debouillis* of the new instruction, founded on the memoirs of M. Dufay, cause the dye to lose in a few instants, if it be spurious, all that it would lose on being exposed during twelve or fifteen days to the air. But as general rules for similar trials must be subject to many exceptions, which are either not foreseen, or being foreseen, cannot be detailed, without running

the risk of causing confusion, or numberless subjects of controversy, it follows that these rules, advanced perhaps as too general, are also too severe in several cases, where light colours admit of salts, or doses of salts, which will be less active than deeply charged dyes, which may lose a considerable quantity of their colouring ingredients in the active liquor of a particular *debouilli*, without exhibiting any very sensible change. It would have been requisite, therefore, to have prescribed a *debouilli* for almost every shade; which was impossible, considering their infinite varieties. Hence the air and the sun will be always the true tests; and whatever colour shall not suffer alteration during a certain time, or shall thus acquire what the dyers call a body, (*fond*,) must be reputed of good dye, even though it should change considerably in the *debouillis* prescribed by the new instruction. Scarlet is an example of this. As soap carries off this colour almost entirely, it was subjected to the proof of alum; and when it is made with cochineal alone, without a mixture of other ingredients, it should assume, in a boiling-hot solution of alum, a purple colour. If scarlet be exposed to the sun, however, it loses a part of its vivacity, and becomes deeper; but this shade is not the one which alum gives it. Hence the *debouillis*, in certain cases, cannot be substituted for the action of the air and sun, at least with regard to parity of effect.

“I have made with brazil wood, which, like all the other woods charged with colour, is a false dye, a much more beautiful red than the madder reds, and as lively as the reds made with the grain of kermes. This red, from its peculiar preparation, of which we shall speak in its place, remained exposed to the air during the last two months of 1740, which were very rainy, and during the first two of 1741. Notwithstanding the rain and the bad weather, it stood; and far from losing, it gained body, (*fond*.) Yet this same red, so solid in the air, does not resist the proof of tartar. Would it be right to proscribe it, because this salt destroys it; or are the stuffs which we employ for our clothing intended to be boiled with tartar, alum, or soap? I do not presume, however, to disapprove of the trials by the *debouillis*. They are useful, because they are speedy. But there are cases where they ought not to serve as rules for pronouncing a sentence of confiscation, especially when



they do not demonstrate that a colour, which ought to have been made with drugs of the *good dye*, has been made with the ingredients of the *spurious dye*."

INSTRUCTIONS *concerning the Debouilli (chemical trials) of Wool and Woollen Cloths.*

"SINCE it has been admitted, that the method prescribed for the *debouillis* of dyes, by Article XXXVII. of the regulations for dyers in the great and good tint, of cloths, serges, and other woollen stuffs, of the month of August 1669,—by the Articles CCXX. and following, of the general instruction for dyeing of wool of all colours, and for the culture of drugs and ingredients used in it, of March 1671,—is not sufficient for judging exactly of the goodness or spuriousness of several colours ; and since this method may even sometimes lead into error, and give rise to disputes, there have been made, by order of his Majesty, different experiments on the wools destined for the fabrication of tapestry, in order to learn the goodness of each colour and its appropriate *debouillis*.

"To attain this object, fine wools have been dyed with all kinds of colours, both in the good and little tint, and they have been exposed to the air and the sun during a suitable period. The good colours stood perfectly well, and the spurious were more or less discharged according to the badness of their quality. Since a colour should not be reputed good, unless inasmuch as it resists the action of the air and the sun, this is a test which has served as a rule for deciding on the goodness of the different colours.

"Different proofs by *debouilli* have afterwards been made on the same woollens, of which patterns had been exposed to the sun and air. It has been observed at first, that the same ingredients could not be employed indifferently in the *debouillis* of all colours, because sometimes a colour found good by exposure to air, was considerably altered by the *debouilli*, while a spurious colour resisted the same *debouilli*.

"These different experiments have shown the inutility of lemons, vinegar, soured waters, and strong waters, (aqua fortis,) from the impossibility of ascertaining the degree of acidity of these liquors. It has therefore appeared, that the surest method

is to make use of ingredients, whose effect is always equal, along with common water.

"In pursuing this object, it has been judged necessary to separate into three classes all the colours of which woollens can be dyed, both in the fast and fading tint, and to define the ingredients that should be employed in the *debouillis* of the colours comprised in each of the three classes.

"The colours comprehended in the first class should be tested with Roman alum; those of the second, with white soap; and those of the third, with red tartar, (argal.)

"It is not enough for ascertaining the goodness of a colour by the trial of the *debouilli*, to employ ingredients whose effect may always be equal; it is requisite, moreover, not only that the duration of this operation be exactly determined, but even that the quantity of the liquid be fixed; because more or less water diminishes or increases considerably the activity of the ingredients which enter into it: hence the manner of proceeding with the different *debouillis* will be prescribed in the following articles.

"Article I.—The *debouilli* with Roman alum shall be made in the following manner.

"Into an earthen or stoneware vessel, one pound of water and half an ounce of alum shall be put: the vessel is to be set on the fire, and when the water boils with large bubbles, there shall be put into it the wool whose trial is to be made, and it shall be allowed to boil there for five minutes, after which it is to be withdrawn and washed in cold water. The weight of the sample ought to be about one gros, (nearly 60 grains troy.)

"Article II.—When there are several samples of wool to be tested together, it will be necessary to double the quantity of water and alum, or even to treble it, which will in no respect change the force and effect of the *debouilli*, if the proportion of water and alum be observed.

"Article III.—In order to make the effect of the *debouilli* more certain, care must be taken not to test together wools of different colours.

"Article IV.—The *debouilli* with white soap shall be made in the following manner.

"Into a pound of water there shall be put only 120 grains of white soap cut into small bits. The vessel being then set upon the

fire, care shall be had to stir the water with a rod, so as to cause the soap to melt properly. When it is melted, and the water is boiling briskly, the sample of wool shall be introduced, and it shall in like manner be made to boil for five minutes, counting from the instant of its being put in, which shall be only when the water boils with large bubbles.

“Article V.—When several samples of wool are to be tested together, the method prescribed in Article II. shall be observed; that is to say, for every pound of water, 120 grains of soap shall be taken.

“Article VI.—The *debouilli* with red tartar shall be made precisely in the same way, with the same doses, and in the same proportions, as the *debouilli* with alum, observing to pulverize the tartar well before putting it in the water, that it be entirely dissolved before the samples of wool shall be put into it.

“Article VII.—The following colours shall be tested with Roman alum; namely, crimson of every shade, scarlet of Venice, scarlet of a fire colour, scarlet of a cherry colour, and its other shades; violets and gridelins of every shade, purples, pinks, *jujubes*, pomegranate flowers, blues, slate-greys, lavender-greys, violet-greys, wine-greys, and all other similar shades.

“Article VIII.—If, contrary to the articles of regulation concerning dyes, there has been employed, in the dyeing of fine wools crimson, ingredients of the spurious tint, the infringement will be easily recognised by the *debouilli* with alum, because it renders fine crimson only a little deeper, that is to say, makes it verge a little towards the gridelin hue; but it destroys the lightest shades of false crimson, rendering them of a very pale flesh colour, and even blanching almost entirely the deep shades of false crimson. Hence this *debouilli* is a certain means of distinguishing the spurious crimson from the true.

“Article IX.—The scarlet of kermes or grain, commonly called scarlet of Venice, is in no respect injured by this *debouilli*. It causes scarlet of a flame colour, or of cochineal, to pass to a purple hue, and strengthens the low shades, so that they get a gridelin tinge; but it carries off almost the whole false colour of brazil, and reduces it to an onion-skin hue. It has a still more sensible effect on the deep shades of this false colour.

“The same *debouilli* also carries off almost entirely the scarlet dyed with *bourre* and all its shades.

“ Article X.—Although violet is not a simple colour, but is formed of blue and red hues, it is, nevertheless, so important as to merit a particular examination. The same *debouilli* with Roman alum has almost no effect on the fine violet, whereas it greatly injures the spurious; but it will be observed, that its effect is not always to carry off equally a large portion of the false violet hue, because this has sometimes a ground of pastel or indigo. This ground being of good tint, is not carried off by the *debouilli*; but the redness is effaced, the brown shades becoming almost blue, and the pale ones of a disagreeable wine-lees colour.

“ Article XI.—With regard to half-fine violets, prohibited by the present regulation, they shall be put in the class of spurious violets; nor do they stand the *debouilli* any better.

“ Article XII.—The fine gridelins will be distinguished in the same manner from the spurious, but the difference is slight. Gridelin of good tint loses only a little less than that of spurious tint.

“ Article XIII.—Fine purples resist the *debouilli* with alum perfectly; whereas the spurious lose the greatest part of their colour.

“ Article XIV.—The colours of pinks, *jujubes*, pomegranate-flower, will incline towards purple after the *debouilli*, if they have been made with cochineal; whereas they will become considerably paler if fustet has been employed, the use of which is prohibited.

“ Article XV.—The blues of good tint will lose nothing in the *debouilli*, whether the colour be pastel or indigo; but those of spurious tint will lose the greatest part of their colour.

“ Article XVI.—Slate-greys, lavender-greys, violet-greys, (reddish greys?) wine-greys, lose almost their whole colour if they are of spurious tint, whereas they will stand perfectly if they are of good tint.

“ Article XVII.—The following colours are to be tested with white soap: namely, yellows, jonquilles, lemons, oranges, and all the shades which are derived from yellow; all the shades of green, from yellow-green, or nascent green, (pomona-green,) to cabbage or parrot-green; madder-reds, cinnamon, snuff-colour, and other similar hues.

“ Article XVIII.—This *debouilli* shows perfectly if the yel-

lows and their derivative shades are of good or spurious tint; for it carries off the greatest part of their colour, if they are made with Avignon berries, annotto, turmeric, fustet, or saffron, the use of which is prohibited for the fine dyes; but it does not affect the yellow made with *sarrette*, (saw-wort,) *genestrolle*, (dyer's broom,) fustic, (yellow-wood,) weld, and fenugreek.\*

Article XIX.—The same *debouilli* will also show perfectly well the goodness of greens; for those of spurious tint lose almost all their colour, or become blue, if they have a ground of pastel or indigo; but those of good tint lose scarcely any of their hue, and continue green.

Article XX.—The reds of pure madder lose nothing in the soap *debouilli*, becoming, in consequence, only more beautiful; but if brazil wood is mixed with it, they lose some of their colour in proportion to the quantity of the latter which has been introduced.

“Article XXI.—Cinnamon, snuff, and other similar colours, are scarcely affected in the *debouilli* if they are of good tint; but they lose a great deal if annotto, fustet, or *font de bourre* have been employed in it.

“Article XXII.—The *debouilli* made with alum would be of no utility, and might lead even into error, with regard to several colours of this second class; for it does not injure fustet or annotto, which do not however withstand the action of the air; and it carries off a portion of saw-wort, and dyer's broom, which give, however, very good yellows and very good greens.

“Article XXIII.—All the fawns, (duns,) or root colours shall be tested with red tartar. Thus, all those colours are termed which are not derived from the five primitive colours: such colours are made with walnut peel, the root of the walnut tree, alder tree bark, sumach, or *roudoul*, sanders and soot. Each of these ingredients affords a great number of different shades, which are all comprised under the general name dun, or root colour.

“Article XXIV.—The ingredients enumerated in the preceding article are good, with the exception of sanders-wood and

\* The botanical names of the above vegetable substances are as follows: *Rhamnus infectoria*, (French or Avignon berries;) *bixa orellana*, from which annotto (*rocou*) is made; *curcuma longa*, turmeric (*terra merita*;) *rhhus cotinus*, fustet; *cracus salivus*, saffron; *serratula tinctoria*, saw-wort (*genet*;) *genista tinctoria*, dyer's broom; *morus tinctoria*, fustic; *reseda leuteola*, weld; *trigonella fenugracum*, fenugreek.—T.

soot, which are a little less so, and which make woollens harsh when too large a quantity is taken. Hence, all that the *debouilli* can teach concerning these kinds of colours is, whether they have been surcharged with sanders-wood or soot, in which case they lose considerably by the *debouilli* of tartar; and if they are made with other ingredients, or if there be but a moderate quantity of sanders-wood or soot, they stand much better.

“Article XXV.—As black is the only colour which cannot be comprehended in any of the three classes above stated, and since it is necessary to make use of a *debouilli* much more active, in order to learn whether wool has had the deep blue ground conformably to regulation, the *debouilli* shall be made in the following manner:—

“One pound or one pint of water shall be taken: into this shall be put one ounce of Roman alum, and as much pulverized red tartar; the whole shall be made to boil, and a sample of wool shall be introduced, which ought to be kept boiling briskly during a quarter of an hour. It is to be thereafter washed in fresh water, when it will be readily seen whether it has had the proper blue ground; for in this case the wool will remain of a blue, nearly black; if that be wanting, it will become considerably grey.

“Article XXVI.—As it is the practice to brown colours sometimes with nut-galls and copperas, and as this operation, called browning, (*bruniture*), which should be permitted in the good tint, may have a peculiar effect on the *debouilli* of these colours, it will be observed, that although after the *debouilli* the bath appears charged with the dye, because the browning has been carried off, the wool will be not the less reputed of good tint, if it has preserved its body. If on the contrary it loses this, it will be declared of spurious tint.

“Article XXVII.—Although the browning given with copperas and nut-galls be of good tint, as it usually renders wool harsh, it will be proper, as far as possible, to employ the indigo or pastel vat in preference.

“Article XXVIII.—The ordinary greys made with gall-nuts and copperas should not be subjected to any trial of *debouilli*, because these colours are of good tint, and are not made otherwise. But it must be observed to gall them first, and to put

the copperas into a second bath, not nearly so hot as the first, because in this way they are finer and more fixed."

From the remarks of Hellot, it appears, that there has been heretofore only one certain manner of ascertaining the permanence of colours, namely, exposing them to the air, the sun, and moisture for an adequate length of time. The *debouillis*, whatever care be taken to make a good choice of them, can be applied only to determinate processes, such as those prescribed by the regulations to which they were to be subjected. One of these *debouillis* might, however, be excepted, that which is applied to black, with a view of determining whether a blue ground has been given, and whether it be strong enough to inspire confidence in the goodness of the dye.

"The chlorine affords a ready and easy means of determining the degree of permanency of a colour. Hence, when a colour is wished to be examined, a sample of the stuff has only to be put into the chlorine, along with a sample of a like colour which had been dyed by a good process. The degree of resistance which the colours of the two samples oppose, becomes the measure of their goodness; but as this liquor has a very lively action on the colouring particles, it must be employed in a very dilute state. This proof has the further advantage of making known, pretty nearly, the shades and degradations through which the stuff is to pass, when it shall be altered by the air; were it required, however, to examine a stuff juridically, the action of chlorine could not be entirely trusted to; nor would it be possible to pronounce with certainty, unless from the results afforded by exposure to the air."

We extract this passage from the first edition of the Elements of Dyeing, because Bancroft has objected to the testing of colours by chlorine, as being entirely illusory and deceitful. We persist in the opinion, that this easy test may be useful, especially in experiments on dyeing; and that it rarely affords false indications when the precaution is taken which has been prescribed of comparing two samples of the same colour, one of which has a known durability; but we might be led into error, if we wished to make the comparison of different colours with one another. We should run the risk, for example, of ascribing to yellows and fawns a greater comparative solidity than they

really possess in the air; because chlorine giving this hue to substances of an animal nature, this effect might be easily confounded with the preservation of these colours.

For trying colours on silk, it is usually held satisfactory to expose them to heat in acetic acid or in lemon juice. They are regarded as permanent and fine if they resist this trial; and in fact, when woods or archil are simply made use of, the colour passes to red by the action of the vegetable acid; but if the solution of tin has been used in dyeing with these substances, the colour which had been prepared in an acid liquid is not affected by the vegetable acids; and in this case a colour might be regarded as fine, which had cost much less for its preparation, and which is easily altered. Hence, with regard to silk, chlorine must be had recourse to, or above all, exposure to the air.

As to cotton and linen goods which are intended to be submitted to soap and leys, they must be tried by the action of soap and alkalies.

There is another species of test which ought not to be neglected; the purpose of which is to determine the goodness of colouring substances of the same nature. The look, and some other criteria, are generally trusted to; but they afford only uncertain estimates, and can furnish no scale of comparative value. Chlorine possesses this property in a degree which leaves nothing to be desired; because, whenever indigo is compared with indigo, the nature of the colouring particles is the same, or nearly the same, and no foreign affinity prevents the action of chlorine from determining the proportional quantity of colouring matter.

If an inconsiderable difference existed between the nature of the colouring particles that were assumed as the same, it is very probable that the action of chlorine would be, moreover, a measure of their respective goodness.

Whenever, therefore, it is wished to compare two or several substances which have the same colour, and to determine their quality or value in reference to the purpose for which they are intended, it is necessary merely to compare the quantities of the same chlorine requisite to reduce an equal weight of each of these substances to the same degree of destruction; then the qualities of these substances, or the quantity of colouring particles which they contain, are in direct proportion to the measures



of liquid which have been necessary to produce the same effect upon each. For making this valuation, the colouring particles of each substance ought to have been dissolved in a proper liquid, and every substance of the comparative operation should be equal.

If it is desired to compare several species of indigo, for example, an equal weight of each is taken, and pulverized with care; they are then put into separate matrasses, with eight times their weight of concentrated sulphuric acid. The matrasses are kept in a heat of from 100° to 120° Fahr. for a few hours. Each solution is afterwards diluted with the same quantity of water. The liquids are filtered; and the *residua* collected on the filters being bruised in a glass mortar, with the addition of a little sulphuric acid, they are left again to digest. These last solutions are diluted with an equal quantity of water, then filtered, and added each to its correspondent liquor. Lastly, into each solution there is poured the quantity of liquid chlorine which is requisite to destroy its colour, or rather to bring it to the same shade of yellow. The qualities of the different species of indigo are proportional to the measures of chlorine which was needed to destroy their colour.

The tests for colouring particles soluble in water are much more simple. After exhausting them, equal volumes of the decoctions of the same weight of these substances are taken; and then the quantities of chlorine necessary to bring them to the same tint, are compared.

## SECTION V.

### OF THE CHEMICAL AGENTS EMPLOYED IN DYEING.

IN order to form an exact idea of the effects produced by the substances employed in dyeing, their chemical properties must be known, for these effects are merely consequences in particular cases.

We shall here present a summary view of the history and properties of the substances most commonly used in dyeing, and in the arts immediately related to it, stating, at the same time, the general principles which may serve to explain their action.

We shall so arrange it, that those persons who have but a limited acquaintance with chemistry, may find in this summary the most useful notions, and that those who are further advanced in the speculations of the science, may perceive the relations connecting the particular phenomena to the general laws of combination.

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## CHAPTER I.

### *Of the Acids.*

THE acids are recognised by their taste, their property of reddening the blue colour of several vegetables, such as that of litmus, flowers of mallow, and violets, and by the effervescence which they produce when mixed with mild calcareous earth and alkalies. But these characters being merely a consequence of their action, afford no idea of the properties by which they act in the production of these very effects.

All the chemical properties of a substance depend on its affinities to other substances: but the effects of an affinity

differ according to the physical dispositions of the substance which exercises it, and of that on which it exerts its action. The latter acts reciprocally on the former by its affinity, and according to its physical dispositions.

The affinity by which two substances form a combination, in which their properties have become more or less latent, produces an effect dependent not only on its energy, but also on the quantity of the substance exercising it.

In proportion as an affinity is satisfied, or as it experiences saturation, its energy diminishes; and when it is exactly counter-balanced by the action of the substance that produces saturation, the combination is neutral, or affords no farther indication of the action peculiar to each of the elements which compose it.

The substances which produce in the highest degree the saturation of the characteristic properties of the acids, and which make them entirely disappear, are the alkalies, whose properties experience, on their part, a like saturation. The reciprocal action of these substances is thereby capable of even disclosing the laws of chemical action, or of the tendency to combination.

The acidity, or the power of combination of the different acids with the alkalies, should therefore be proportional to the quantity of the same alkali which they can saturate, or to their capacity of saturation; and reciprocally.

The physical qualities of the substances diversify the effects of affinity. We understand here by physical qualities, all such as do not depend on the tendency of a substance to form with another a combination whose weight results from the two, although some of these qualities be still derived from affinity; for example, solidity, which is a result of the reciprocal action of the molecules of any one substance, whether simple or compound.

Those physical qualities which change the results of affinity are principally solidity, liquidity, expansibility, or the disposition to assume or retain these different states. They do not disappear by the action of affinity; they thence experience no saturation; but they receive modifications from it, while they themselves act as forces which contribute to the immediate effect of affinity, or which are opposed to it.

The disposition to solidity determines the combinations which

precipitate when an acid is mixed with an alkaline solution, and similarly when several acids and several alkalies exercise a reciprocal action; whence proceed the precipitates or the salts which separate by crystallization. This disposition is increased by the approximation or condensation which affinity produces; and the compound which separates in consequence, readily acquires an excess of the element in which this quality predominates. Hence two substances possessing liquidity, may form an insoluble combination, or a salt less soluble; and the compound which separates may preserve an excess of acid or of alkali, according as one or other of these has a greater disposition to solidity. Thus may be explained the precipitations produced by the acids or the alkalies, and the formation of acid or alkaline salts.

Heat, whose function it is to dilate bodies, and separate their particles, diminishes insolubility, and increases the tendency to the liquid state. It augments especially the disposition to elasticity; and as the latter exercises a force contrary to the tendency to combination of a fixed substance, with a substance possessing the elastic condition, it is obvious, that by increasing it to a sufficient degree, the whole effect of the tendency to combination may be destroyed. If several acids and several bases exert a reciprocal action by the same means, the most volatile elements will be determined to form a compound, which will separate by volatilization from that contracted by the more fixed elements.

The acids act, therefore, by their affinity or tendency to combination, in the ratio of their capacity of saturation; and the physical qualities of their compounds depend on those of the elements composing them, and of the modifications produced on them by the condensation due to the combination, or the expansion which is the effect of heat.

When an acid acts on a neutral combination, the base divides its action in the ratio of the quantity of the two acids, and of the energy of their affinity; but the result depends principally on the dispositions to the solid, liquid, or elastic state of the elements which are in action. The capacity of saturation of two acids usually differs too little to produce an effect capable of counterbalancing one of the causes just designated.

Hence, when an acid which has a certain fixity (sulphuric

acid for instance) acts on a muriate whose acid is volatile, the latter ought to be expelled, especially by increasing its elasticity with heat, although it has a greater capacity of saturation for soda.

From the physical qualities of two substances which enter into combination, may therefore be inferred those which subsequently exist in the compound itself; and as the same causes act when there is a rivalry of different acids for one base, or of different bases for one acid, or of several acids for several alkalies, there will be found, in considering the qualities of each of these substances, the reason of the peculiar compounds which separate by precipitation or volatilization, or which remain liquid, and of the changes that different temperatures may produce on these combinations.

The acids and alkalies exercise a pretty powerful action on most of the colouring substances. We have shown that the results of this action are, more soluble compounds with such of these substances as have in themselves greater disposition to solubility. Thus the acids act in general. But we have remarked, that the crystals of tartar retain the colouring matter of cochineal. Potash, soda, and ammonia, act also as solvents; while the slightly soluble alkalies, lime, barytes, and strontian, form insoluble compounds. Few experiments have hitherto been made in this point of view.

Some acids act on colouring substances by the oxygen which enters into combination with them, or with their elements. This subject has been already sufficiently discussed.

Neutral salts possess but a feeble action on colouring particles; they change their solubility little; and they produce but a moderate effect on their shades. Sometimes, however, this effect is taken advantage of when they are employed as alterants.

### I.—Of *Sulphuric Acid*.

Pure sulphuric acid is without smell or colour, transparent as water; and when concentrated it is of an unctuousity approaching to that of oil. To denote this unctuousity, it was called *oil of vitriol*, a designation which may lead to dangerous mistakes concerning its nature.

This acid was at first extracted from the sulphate of iron, or

vitriol of iron, whence its old name of vitriolic acid. At the present day, nearly the whole that is employed in the arts is obtained from sulphur, by a much less expensive process. It is the result of the combustion of sulphur, which, by burning, combines with the oxygen present in the atmospheric air, and in the nitre which is added to a certain quantity of the sulphur before setting it on fire. The latter, however, seems to be especially useful for exciting the high temperature necessary to the formation of sulphuric acid; for it has to enter into the composition of the sulphate of potash produced. The mixture of sulphur and nitre is kindled, and its vapours are received in a leaden chamber, whose bottom is covered with a stratum of water. The vapours which collect and unite to the water, form the sulphuric acid, which should be considered as sulphur completely burned. (NOTE V.)

The sulphuric acid, as it comes out of the leaden chamber, is not in a concentrated state, but is mixed with a certain quantity of redundant water. It retains the odour of sulphurous acid, which differs from sulphuric acid in its composition; as the former is not sufficiently saturated with oxygen, while this element is less condensed in it. It retains also a little nitrous acid, proceeding from the nitre mixed with the sulphur. If it be left for some time exposed to the air, the smell of sulphurous acid is dissipated. But another method is employed to deprive it of odour, and at the same time of a portion of its redundant water. It is evaporated with heat.

Only a very small quantity of vegetable or animal substance is required to give this acid a brown colour; and the acid of commerce has rarely a very clear colour. But this limpidity may be obtained by boiling it for some time in a retort. By this operation it is deprived at once of a portion of nitric acid usually present, and of a portion of water which it had retained. It becomes white and transparent; the concentration being the greater the more water has been driven over by the distillation. To procure it of thorough purity, we must, after having separated the first portion, which is impure, and feebly acid, continue the distillation till no more liquid remains in the retort. The residuum consists of a little alkali derived from the nitre, which remains combined with an excess of sulphuric acid; a combination named acidulous sulphate of potash; sometimes a little sulphate of lead is also left.

For this rectification, there must be selected a retort not very lofty, which is to be well secured in an open furnace, or placed in a sand bath, so that the movements occasioned by the ebullition of the acid may not break it.

Sulphuric acid powerfully attracts the humidity of the air. To preserve it concentrated, it must therefore be kept in glass vessels carefully stopped.

When it is mixed with water, a great heat is produced. Hence this mixture should be gradually made, to prevent the fracture of the vessel, an accident which is avoided by making the mixture in a leaden vessel. In order to effect a complete mixture, the liquid must be long stirred with a glass rod; for notwithstanding the great affinity of this acid for water, the difference of their specific gravities opposes their combination.

The difference of volatility, and the mutual action of the sulphuric acid and water, explain the effects which arise from this action in different circumstances. It attracts water, causing the moisture which is held dissolved in the atmospheric air to lose its elasticity; and it is only by increasing the elastic disposition of the latter by heat, that it can be again separated. But to reduce the water into vapour, a greater heat is required than if it were not retained by the affinity of the acid; a heat which must be augmented according as the proportion of water diminishes. Lastly, the acid passes over itself in the distillation along with a decreasing proportion of water, which must in its turn promote this effect by reason of its volatility.

The fixity of this acid, its concentration, the property it has of freezing, show that it must carry into its combinations a great disposition to insolubility, when the base has the same disposition. Hence it produces slightly soluble combinations with lime, barytes, strontian, and several metallic oxydes.

The condensation of sulphuric acid proves that the combination of oxygen with sulphur is here very intimate, and consequently it should not easily part with its oxygen. For this reason, it produces no decomposition of the colouring substances which it dissolves, unless this solution be exposed to a strong heat. Then the hydrogen and the carbon of these substances may combine, particularly with a portion of the oxygen of the acid, which is thereby brought to the state of sulphurous acid, which, being volatile, escapes in the progress of the

decomposition. As the oxygen is endowed with greater elasticity in the latter acid, it abandons the sulphur more easily, though this substance be in larger proportion than in sulphuric acid.

Sulphurous acid, therefore, acts on colouring substances, by giving up oxygen to them less easily and less efficaciously than nitric acid, or chlorine; but in other circumstances, it may carry off even oxygen, as it does on being mixed with chlorine.

Highly concentrated sulphuric acid has a specific gravity, nearly double of that of distilled water. When it is weak, that is, diluted with a great deal of water, the fallacious name of *spirit of vitriol* has been given to it.

In order to obtain uniform effects, it is right to employ for the same operations, a sulphuric acid which has always the same degree of concentration. Its specific gravity must be therefore ascertained, which is commonly done by means of the areometer of Baumé. For this purpose, the acid is put into a glass cylinder, and the areometer for salts is plunged into it. The denser the liquid, the less the areometer sinks, and the degree on that part of its scale which rests at the surface of the liquid, indicates its concentration. Sulphuric acid is regarded as highly concentrated when it is at 66° of this areometer. (Sp. gr. 1.848, or 166° Tw.)

Hitherto sulphuric acid has been used in dyeing, principally for making solutions of indigo; for which purpose it must be strongly concentrated, and very pure. But a great deal of it is employed for preparing cotton goods intended to be printed, as well as for the bleaching of cloths and yarns, whether by chlorine, or by exposure on the grass.

These latter purposes do not require a concentrated sulphuric acid. If therefore a manufactory of sulphuric acid exist in the neighbourhood, it is more advantageous to purchase it before being concentrated, and thus avoid the cost of this operation. But if such an establishment be at a distance, the diminution of the expense of carriage may render it more profitable to purchase it in a state of concentration, than if it were diluted with a certain quantity of water.

## II.—Of Nitric or Nitrous Acid.

Chemists have given different names to this acid, according



to the processes by which it is extracted from nitre. What is obtained from a mixture of nitre and clay is called *aquafortis*; that procured from nitre distilled with sulphate of iron, *spirit of nitre*; and the *fuming nitrous acid* is derived from a mixture of nitre and sulphuric acid: These distinctions are not made in commerce, but the name *aquafortis* is usually given to this acid, whatever process may have been employed. In fact, it is always the same acid, differing only in the degree of concentration, and in colour. It is sometimes white, sometimes red and fuming. The colour and property of fuming, are owing to the nitrous gas which it holds in solution, as we shall explain hereafter.

If the reddest acid be exposed to a sufficient heat, the nitrous gas is disengaged, and the acid remains white. In this state it is called *nitric acid*, while the name *nitrous* is given to the red acid.

As there is no great consumption of this acid in dyehouses, and as these are often at a great distance from the places where the acid is manufactured, it may often be useful and economical to prepare it one's self. This motive induces us to describe here the process by which it is extracted from nitre by means of sulphuric acid.

Pure nitre, called nitre of the third boiling, being the result of a third crystallization, is pulverized, and put into a retort with half its weight of concentrated sulphuric acid, or a little more, in such a manner that one-half of the capacity of the retort remains empty, in order that the materials in boiling up shall not pass over into the receiver. To the neck of the retort a bent tube is adapted, whose orifice must be sufficiently large to embrace and receive it. The other end of this tube, which ought to have a much smaller diameter, is introduced, through a cork, into a receiver with a double neck. To the other opening of this receiver a tube is also adapted, which terminates in a little water contained in a matrass. The communication of the retort with the first tube, and the openings of the first receiver, must be carefully coated and covered with fat lute, consisting of pulverized white clay, boiled linseed oil, and a little litharge. This lute must be beaten for a long time in a mortar, to render it smooth and ductile. The lutings must be wrapped round with strips of linen cloth soaked with white of egg, and be dusted with powdered quick-lime. It is of advantage to have a tubu-

lated retort to prepare the whole apparatus, before introducing the sulphuric acid into it by the tubulure, and even to dilute the sulphuric acid previously with a certain quantity of water.

The second matrass should maintain a free communication with the air, that the vapours incoñdensable in water may escape. The quantity of water put into the second vessel must bear a proportion to the quantities of materials operated upon. The fire must be nicely tempered at the beginning, and be gradually augmented up to the end of the operation. The acid which is obtained in the first receiver is highly concentrated; that which is in the second is weakened by the water put into it for condensing the vapours. The colour of the latter acid is blue or green; colours owing to the nitrous gas; their diversity depending on the proportion of water. Thus, if a little water be added to that which is green, it becomes blue; and when the gas is expelled by heat, the liquor remains colourless. The acid of the second matrass is always pure, but that of the first contains sometimes a little sulphuric acid, arising from the heat not being rightly regulated at the commencement of the operation. For, when tempered with discretion, a perfectly pure acid may be obtained, if the sulphuric acid does not exceed the half of the weight of the nitre.

It is of importance to test the nitric acid of commerce, because a considerable quantity of sulphuric acid is frequently present in it, whether it may have come over in a distillation negligently conducted, or have been added to the nitric acid in order to augment its specific gravity. For testing it, we dilute it with an equal weight of distilled water, and then drop in a little of the solution of nitrate of barytes. If the acid which we try contain sulphuric acid, a precipitate takes place, because this acid forms an insoluble salt with barytes. Nitric acid may likewise contain some muriatic acid, proceeding from the sea-salt which might exist in the nitre employed. This mixture cannot be prejudicial to the operation of dyeing. If, however, we desire to discover it, the acid must in like manner be mixed with distilled water, and a nitric solution of silver is to be then poured into it. A precipitate occurs if muriatic acid be present.

To deprive the nitric acid of the sulphuric, it must be redistilled from a little nitre, or solution of lead may be added to it, which produces a precipitate that is to be separated. After

this, the acid is submitted to a new distillation. By this operation the nitric acid is separated, not only from the sulphuric acid, but also from the muriatic which it may contain. To accomplish the latter object entirely, the first portion of liquid that comes over must be removed, because it may contain some chlorine.

Nitric acid may serve for several metallic solutions, whose use as mordants may be various, but its principal employment is for aqua regia, or nitro-muriatic acid, which shall be treated of in a particular article. It appears that sulphuric acid is injurious to it, when it is to serve for the solution of tin; and the acid prepared in manufactories, by means of the sulphuric, usually contains some; whence dyers often prefer that extracted by the agency of clay.

For understanding a great number of phenomena, it is essential to have an exact idea of the nature of the nitric acid, and of the action which it exercises on other substances.

Nitric acid is composed of two substances, which, when they are insulated, assume the elastic, aeriform, or gaseous state. These substances are oxygen and azote, which also compose our atmosphere. The different action (of these two compounds) depends on the state in which they exist. In the atmosphere they are endowed with elasticity, which is an obstacle to their combination with other substances; but this obstacle, and the intensity of their action, vary, by reason of their state of expansion and their condensation.

The elastic force of oxygen gas, and azotic gas, like that of other gaseous substances, being diminished by the affinity which produces their combination, and which reduces their volume, they can act in a greater mass on the other substances, and the energy which they thereby acquire may exceed by much the diminution which results from their reciprocal saturation.

But these two gases may contract an union, which differs according to their proportions, according to the condensation derived from it, and according to the concurrence of other substances, and particularly of water, which may augment their condensation without acting on them by a great saturation.

These circumstances determine the different states of combination of these two elements, and the properties of these compounds.

Nitrous gas must be regarded as the first state of combination. It dissolves in only a small quantity of water; it does not combine with alkalies; it is easily decomposed by substances which tend to unite with oxygen; but it unites by mere contact with a greater proportion of oxygen. It thereby passes to another state; and as its two elements are little condensed, the action of heat alone, or the dilatation which it produces, has but little efficacy to separate them. The proportions that constitute it are nearly 44 parts by weight of azote to 56 of oxygen, (47 to 53.)

When an oxygenable substance deprives the nitrous gas of a portion of its oxygen, such as a sulphite, which thereby passes to the state of a sulphate, another combination is established, in which the elements, by reason of the proportions in which they exist, exert more powerfully their reciprocal action, so that their condensation is greater. This is the gaseous oxyde of azote, whose specific gravity, according to Davy, is to that of oxygen gas in the ratio of 147 to 100; and which contains, by the determinations of the same chemist, 63 parts by weight of azote to 37 of oxygen.

This greater condensation, which proves a stronger reciprocal action, and the composition, explain the properties which characterize this gas. It dissolves more copiously in water than the nitrous gas, and yet it has no acid taste, but on the contrary a saccharine one. The oxygen present in it, is too strongly saturated by the azote, to produce the acidity which depends on its combinations. It no longer acts on oxygen gas, and is not decomposed at an ordinary temperature, by the substances which operate the decomposition of nitrous gas; but if the temperature be elevated, the expansive action of the heat, which tends to separate its two condensed elements, determines its decomposition, and the oxygen produces a vivid combustion.

When nitrous gas acts on pure oxygen gas, or on that present in the atmosphere, it becomes ruddy, and the new substance designed by the name *nitrous vapour*, which condenses very little, and preserves a livelier ruddiness, as the temperature is higher, forms another combination when it is placed in contact with water. This decides the formation of nitric acid, of which it is itself an essential part; for nitric acid resumes the state of nitrous vapour when it is deprived of water, unless it be

retained in a state of condensation by another base, as in the nitrates.

If nitrous vapour contain too great a proportion of nitrous gas, this excess remains in the gaseous state; if the oxygen gas be in excess, a portion of it remains gaseous.

A portion of the nitrous gas may, however, be held in solution by the nitric acid; but this quantity varies according to the proportion of water, giving the acid an orange, green, or blue colour. This excess of nitrous gas attracts oxygen by degrees from the atmospheric air, passing itself to the state of nitric acid.

In nitric acid, the proportion of oxygen is to that of azote nearly in the ratio of three to one by weight. It is not surprising, therefore, that this compound, containing oxygen in so large a proportion, should have the qualities of an energetic acid, whilst the gaseous oxyde of azote, where the azote predominates, has perceptibly none. But the nitric acid owes its liquid state only to the action which water exerts upon it.

When it is combined with an alkaline base, and when a more fixed acid, as the sulphuric, divides its action on this base, heat augments its elastic disposition, so as to volatilize it with the water which the sulphuric acid contained. This water is inadequate to make the whole of it preserve the acid condition; a portion is therefore disengaged in the state of nitrous vapour, and by the condensation of this in the water presented to it, some nitric acid is reproduced. But the acid which has assumed the liquid state, retains nitrous gas, and is more or less ruddy. The corresponding portion of the oxygen gas is disengaged in the elastic state.

If nitre, or nitrate of potash, be decomposed by means of clay, this seems to retain the water with sufficient strength, so that a quantity of it, capable of maintaining the nitric acid in the liquid condition, may come over even to the end of the operation. Hence, in this case, the acid is not fuming, or is very slightly so.

The substances which have a great action on oxygen, may decompose nitric acid, according to the energy of this action. Thus the very oxydable metals especially, produce gaseous oxyde of azote, while the oxyde thereby formed dissolves in a portion of the undecomposed acid. But the less oxydable metals

give rise only to nitrous gas, which retains a greater proportion of oxygen.

The facility with which nitric acid is decomposed, when it is not condensed by a base which gives it stability, renders it little fit for being employed with the colouring particles, which separate the oxygen from it more or less speedily, and thereby suffer destruction. In destroying these particles, it causes them to undergo the changes due to an imperfect combustion, in which the hydrogen enters into combination with the oxygen, in larger proportion than the carbon, making the latter principle predominate in the residuum.

In purchasing this acid, we must not let ourselves be imposed upon by its more or less ruddy colour. It is easy to give it this appearance, by a small quantity of iron, or other substance, which generates nitrous gas. It must, indeed, have a certain degree of concentration to be fuming; but it may be highly concentrated without possessing this appearance.

The specific gravity may likewise lead to fallacies, because it can be increased by the addition of sulphuric acid. It is only after ascertaining that this cause of error does not exist, that we can repose confidence in that criterion.

### III.—Of *Muriatic Acid*.

Muriatic acid is particularly distinguished by being more volatile, or more disposed to preserve the gaseous state, than the preceding acids, and by having much less affinity for water. Hence, when combined with it, its elastic action needs only be increased by heat for it to quit it, and to resume the state of gas, till little enough remains to make the attraction of the water be equivalent to the elasticity of the acid.

Although muriatic acid has a greater capacity of saturation for the alkaline bases than sulphuric acid, it is however expelled from its combinations by this acid, especially when its elasticity is augmented by heat. Hence the effect of its elasticity overcomes the excess of affinity, which tends to maintain its combination with the base.

Muriatic acid gas, combined with water, forms muriatic acid, which was known under the name of *marine acid*, or *spirit of salt*. It has a peculiar odour, analogous to that of saffron.

When concentrated it gives white vapours to the air, which are produced by the combination of this acid with the water present in the atmosphere. It ceases to afford these vapours at the point in which it is saturated with the whole water which it can take from the atmosphere. It has usually a yellow colour, derived from a little iron, or chlorine, for when very pure it is as colourless as water.

This acid is extracted on the great scale from sea salt, or muriate of soda, distilled along with clay. But by this process it is always weak. It is disengaged from the same salt by means of sulphuric acid.

This process has much resemblance to that described under nitric acid; but there are some differences which depend on the greater volatility of the acid.

A tubulated retort is made use of, or which is preferable, a large matrass, to whose orifice there is adapted a tube bent in its middle, with an enlargement in the lower part of its curvature. By this tube the sulphuric acid is introduced, a portion of which being retained in the curvature and the swelling, serves to stop the issue of the gas, whose pressure disturbs only the level at which it stands in the two branches of the curvature. The obstacle resulting from the elevation of the column of sulphuric acid, determines the gas, therefore, to pass off by a conductor tube, where it finds less resistance.

The salt is first introduced into the matrass; after which there is poured in three-fourths ( $\frac{3}{4}$ ) of its weight of sulphuric acid, which should be previously diluted. The rest of the apparatus should have been also arranged beforehand. It consists of two bottles, into which is distributed a weight of water equal to that of the salt employed. But as the vapour which is disengaged unites speedily with the water, a vacuum is readily formed, which makes the liquid of the second bottle pass back into the first, and from the first into the retort. To prevent these re-absorptions, the first bottle ought to be furnished with the tube of safety contrived by Welter. This tube is introduced into a particular tubulure, or still better through one of the corks which gives passage to a tube of communication. If a vacuum be formed, the atmospheric air returns into the bottle; but while the issuing vapour presses on the liquid, this rises in the

tube, till its column counterbalances the compression of the vapour. It is requisite to lute with much care, because the vapours of muriatic acid are very penetrating; and when they have once forced a passage through the lute, it is very difficult to repair it. Should this accident, however, happen, the best means of remedying it is, to rub the outlet with some alkali, so as to saturate the acid, and immediately after to stop it with the lute. It is necessary to wait till the effervescence produced by the affusion of the sulphuric acid be assuaged, before putting fire under the retort, which should be placed on a sand-bath, and the fire should be nicely tempered, especially at the beginning of the operation.

The acid obtained in the first bottle is highly concentrated and smoking, especially if it had been kept immersed in cold water, or pounded ice; but it may contain sulphuric acid, which is discovered by diluting it with distilled water, and pouring into it a little solution of barytes, which produces a precipitate. It may be rectified by distilling it from a little sea salt.

The acid of the second bottle is much less concentrated. If too weak for the purposes for which it is intended, it may be used instead of water in a second operation. It has, however, the advantage of being pure.

Muriatic acid is hardly ever employed directly in the processes of dyeing; but it serves to form metallic solutions fit for making mordants, alone, or in conjunction with nitric acid. Muriate of tin is the combination which deserves most attention. We owe to Pelletier and Proust very interesting observations on this muriate.\* We shall detail such of them as relate to our subject.

To prepare the solution of tin by muriatic acid, Pelletier directs to put one part of tin, and four parts of concentrated muriatic acid in a matrass, placed in a sand-bath, which is gradually heated to ebullition. The heat of ebullition cannot be favourable to the combination of the muriatic acid, on account of the elastic force which it gives it. It seems therefore that a more moderate degree of heat is suitable; but ebullition may be afterwards produced, in order to expel the excess of acid, which may be condensed in a second matrass. We then proceed to crystallize.

\* Mem. et observat. de chimie de Pelletier, tom. i. Proust Journ. de physique, tom. li.



The muriate produced by this process contains the tin in the lowest degree of oxydation requisite for its combination with an acid. In this state it carries off the oxygen, not only from the chlorine and sulphurous acid, but also from the atmospheric air, and from all bodies which do not retain this element with force. Hence, it may obviously be a very proper guide in researches on the properties of colouring substances; and since the oxyde of tin combines easily with stuffs and colouring particles, this muriate may be very useful in the processes of dyeing.

Its effects must vary according to its state of actual oxydation. Pelletier concludes from some trials, that in its most oxydized state it is most advantageous in dyeing. This conclusion is perhaps too general, and we believe that experiments must decide what is proper in this respect for each species of dyeing.

To obtain muriate of tin in the most oxygenated state, Pelletier prescribes the transmission of chlorine into a solution of tin in muriatic acid, till this retains the odour of it; after which the excess of acid must be volatilized by heat. The muriate of tin may be oxygenated by leaving its solution simply exposed to the atmospheric air. But the operation is slow.

It is particularly for cotton and linen that the muriate of tin may be advantageously employed in dyeing, or at least it cannot be used in quantity for substances of an animal nature, because muriatic acid exercises too keen an action on them. This fact is applicable to the other metallic muriates.

The alkaline muriates are used only as alteratives. In general they give a deeper shade to colours.

We have discussed at sufficient length the preparation and properties of chlorine in treating of bleaching. We shall confine ourselves here to some considerations on the properties which distinguish it from the preceding acids, and on the differences thence resulting as to their preparations.

Muriatic acid naturally possesses considerable elasticity; yet the action of water can condense a very large quantity, and give it the liquid state, although it is much less powerful than on nitric and sulphuric acids. It combines with oxygen to form oxygenated muriatic acid, (chlorine.) But this combination is feeble, so that it produces but a slight change on the natural qualities of the oxygen and muriatic gases. Chlorine is much less soluble in water; hence the apparatus for the preparation

of liquid chlorine ought to be so contrived, that the gas may be disengaged in the lower part of the receiver, so as to be retained in contact with the water under a first tub, that that which arrives next may flow out under a second, and lastly under a third tub. Thus, by the length of the contact, the solution requiring longer time as it is effected by a feeble affinity, may have leisure to take place. (NOTE W.)

The apparatus which we have described, and which may be modified in different manners, is adapted to maintain the contact of the gas with the water; but it would be too troublesome and expensive, when chlorine is wanted only for some tests or experiments. In this case, an apparatus similar to what we have pointed out for the preparation of muriatic acid may be substituted. It is necessary to employ merely three successive receivers, or three bottles furnished with their tubes of safety. The conductor tubes, intended to transmit the gas from one bottle into another, must issue from the upper part of the one bottle, and dip into the lower part of the next. If the gas be received into an alkaline solution, two receivers, or even one, may suffice.

Instead of the mixture of muriate of soda and sulphuric acid which we have prescribed, muriatic acid may be directly employed. One part of manganese is then necessary for four parts of concentrated muriatic acid, or for an equivalent quantity of weak muriatic acid; and the latter is preferable on account of the too tumultuous disengagement of gas, produced by the concentrated acid. The heat can hardly be too slowly conducted. The operation should cease whenever the first tube becomes hot. Chlorine acts differently, according to the affinity which the other substances have for the two elements that compose it. If these bodies tend to combine particularly with oxygen, they carry off this element from the muriatic acid, which is retained by the water. Thus light disengages the oxygen, restoring it entirely to its elastic state, while the water retains the plain muriatic acid. Thus, also, the colouring substances take possession of the oxygen, which thereafter exerts its action on such of their elements as have most affinity for it.

The alkalies tend to combine with the two elements of the chlorine, although in some circumstances, the action which they exercise on the muriatic acid determines, by the formation of a

muriate, the separation of a portion of the oxygen, which resumes the gaseous state. But, excepting this effect, the action of the alkalies condenses the chlorine, and, by a necessary consequence, lessens or represses its odour.

When the condensation arrives at a certain degree, the action of the alkalies, becoming proportionally more energetic, decides the formation of two new combinations, one of which is a simple muriate, and the other a chlorate. The oxygen accumulated in the latter undergoes on the part of the alkalies so strong an action, that light and colouring substances can no longer disengage it. The whole of the chlorine, which contributes to the formation of a chlorate, when we receive the chlorine into an alkaline solution, is therefore lost as to the power of discoloration.

The difference of action between nitric acid and chlorine, on colouring substances, and in general on vegetable and animal bodies, depends on the affinity of the oxygen for azote, and for muriatic acid. The first is much the stronger. Hence, nitric acid gives up its oxygen with far greater difficulty; but when the resistance of this affinity is overcome, the results of the action of both are similar.

The same difference is observed in the action of the two acids on the metals. Nitric acid is decomposed only in part by the action of the metals; and while one portion gives up its oxygen, another usually combines with the metallic oxide without changing its nature. But the chlorine is entirely destroyed by the action of the metals. From the metals, merely super-oxidized muriates are obtained; and only alkaline muriates in the precipitation by the alkalies. Hence the denomination of oxygenated muriate of mercury, for example, might give a false idea of this combination, which is merely a highly oxydized muriate of mercury. Oxygenated muriates of the metals may, however, be formed, by combining the chlorine with a metal already saturated with oxygen, as Chenevix has shown. (NOTE X.)

#### IV.—Of *Aqua Regia*, or *Nitro-muriatic Acid*.

To this compound acid, the name *aqua regia* has been given, because it has the property of dissolving gold, which was called

the king of metals. But it should be regarded as a mixture of muriatic acid and nitric acid, which combine their forces to effect solutions which they could not separately do.

By the reciprocal action of these two acids, a portion of the nitric acid is decomposed. Hence results a development of chlorine which exhales, diffusing its odour; and nitrous gas is proportionally formed, which remains dissolved in the compound acid, and which colours it progressively, till an equilibrium of combination be effected. But neither the chlorine which is volatilized as it forms, nor the nitrous gas, which is also expelled whenever the acid exerts its action on another substance, contributes to its action on the metals. As its operation only is considered, the name *nitro-muriatic acid* is retained for it, whatever be its composition.

Nitro-muriatic acid may be prepared, either by simple mixture of the nitric and muriatic acids, or by dissolving muriate of ammonia, or of soda in nitric acid. Other salts might be made use of, for example nitre (nitrate of potash,) which might be dissolved in muriatic acid. Several other processes might be employed, which it is needless to describe.

It is especially for the solution of tin that nitro-muriatic acid is to be examined, because it is the principal use which is made of it in dyeing.

Dyers do not prepare in an uniform manner the solution of tin, to which they give the name of *composition* (spirit.) Every one has his recipe. This solution, however, produces different effects, according to the process made use of. It is essential that the same artisan should prepare it always in the same manner, in order to obtain uniform effects, and to guide himself by the observations which he may have made in the preceding operations.

Several dyers make use merely of the aquafortis of commerce; and it seems, that when they began to employ the solution of tin, they used no other solvent. This aquafortis is a species of nitro-muriatic acid, because there has been employed for its preparation an impure nitre, which is mixed with a greater or less quantity of marine salt. But this quantity varies; and the concentration of the aquafortis is likewise subject to many variations. Hence this acid must produce uncertain effects.

Pure nitric acid dissolves tin only when it is very much weakened, and when care is taken to keep the vessel with the materials in cold water. The metal is, in this case, at the lowest degree of oxydation, according to Proust's observation. But it speedily falls down, even at an ordinary temperature.

Vogler employed a similar solution in dyeing. He prevented the precipitation of the oxyde, by adding muriate of soda or ammonia: but it is better to employ immediately the nitro-muriatic acid, which requires less attention.

When a more concentrated nitric acid is used, or when heat is applied, the tin passes to the maximum of oxydation, and is entirely precipitated. This process is had recourse to for ascertaining the weight of tin which exists in an alloy; the tin having thus taken 40 parts of oxygen for 100 of metal.

Hellot took 32 parts of nitric acid, which he mixed with an equal quantity of filtered water (distilled water?) he dissolved in it, by little at a time, two parts of very white muriate of ammonia, and one part of nitrate of potash; and lastly, two parts of granulated tin. Scheffer dissolved one part of tin in four parts of nitro-muriatic acid.\* Macquer dissolved three parts of tin in eight parts of nitric acid, with which he mixed one part of muriate of ammonia, and six parts of water. Pœrner employed other proportions, &c.

These solutions, so very various, possess undoubtedly different properties. In them all, one essential object is wanting, which is a preparation constantly uniform. For this purpose, it is indispensable to make use of a pure nitric acid, and to determine its specific gravity by means of the hydrometer. The process which was resolved upon, after several trials, in the first edition of these Elements, consists in taking nitric acid at 30° B. (1.26 sp. grav.); to dissolve in it one-eighth of its weight of muriate of ammonia, to add by small portions at a time one-eighth of its weight of tin, and afterwards to dilute this solution with a fourth of its weight of water.

A pure tin, such as the Malacca tin, or good English tin, must be selected; because the common tin (of France) contains copper and lead, metals which would be injurious to the beauty of the colours. Even in the fine tin of England some copper

\* Essai sur l'art de la teinture.

is found; but common tin contains occasionally nearly one-half its weight of lead, and antimony and bismuth besides.\* The tin must be reduced into granulations, by melting it and pouring it into water, which is agitated with a bundle of small rods; an operation which ought to be cautiously made, to avoid explosions.

In the solution of tin, there is usually formed a small blackish deposite, from which the liquid should be decanted.

The solutions which contain a great proportion of tin are brown, and afford deeper and duller colours; yet occasions may be found where they can be useful. One may be obtained highly charged with tin, which may be advantageous in certain cases, by decomposing in a retort, at a very moderate heat, muriate of ammonia, mixed with an equal weight of oxyde of tin. The residuum is dissolved, filtered, and evaporated so as to crystallize. By this means crystals are procured of a triple salt, composed of muriatic acid, ammonia, and oxyde of tin. To make use of this salt, a little muriatic acid must be added to its solution, which prevents the precipitation of the oxyde of tin.

The solution of tin in nitric acid is accompanied by a production of ammonia. We have ascertained that the same production took place, when the solution was effected with the simple mixture of muriatic acid and nitric acid, although it be made with great slowness and precaution, and although the oxyde of tin be only in the lowest state of oxydation. It thence appears, that there must be less difference than might be thought between the action of simple nitro-muriatic acid, and that of the preparation into which muriate of ammonia is put.

It is probable that a new quantity of ammonia is produced in the very process of scarlet dyeing, which is performed at a degree of heat approaching to ebullition.

It has been attempted to explain, by the action of this ammonia, which saturates the muriatic acid, and whose formation contributes at the same time to the destruction of the nitric acid, why the nitric acid does not attack (corrode) wool in dyeing scarlet, which is done at so high a degree of heat, although this acid be very destructive to it when it is insulated.

\* Recherches sur l'étain; par MM. Bayen et Charlard. By common tin, the Author must mean what we call pewter.—T.

In this saturating action has been also seen the explanation of an observation of Bancroft. In dyeing scarlet, he wished to substitute muriate of tin\* for the nitro-muriate; but a larger proportion of it was required, and the wool was found to be deteriorated. In this operation no ammonia could be formed, and the muriatic acid, which weakens the woollen fibre, exerts all its action on it.

Muriate of tin may be more useful for cotton and linen, on which substances muriatic acid has much less action.

No consideration ought to be neglected for varying the mordant best fitted to procure fine colours in dyeing.

The solution of tin assumes more or less quickly the consistence of a jelly. When this occurs, the dyers say that the composition has turned. For avoiding this, it is proper to make the preparation only a short while before it is to be used. When the jelly is merely beginning to form, the solution may be restored, by adding a certain quantity of muriate of soda. This inconvenience proceeds from the tin continuing to get more oxydized by means of the oxygen which it attracts from the atmosphere, or receives from the nitric acid; and from a greater quantity of ammonia being formed, which, rendering the tin insoluble in the acid, causes it to precipitate. Heat promotes this effect; hence the solution of tin does not keep so long in summer as in winter.

Uniform observation has taught, that when the solution of tin is briskly made with the copious evolution of vapours, the colours obtained from its employment are less lively and less agreeable, than when the solution is made slowly and without effervescence. Hence, at least for the dyeing of wool, tin should be at the lowest stage of oxydation. It does not remain in this state; and it seems to pass to a more advanced degree of oxydation in the very operation of dyeing. It would not otherwise afford a white basis to the colour. But this circumstance is undoubtedly advantageous. It is a reason for preferring solutions which are recent, and made with slowness, to those which are old, with whatever care they may have been prepared.

Haussman has recommended, for some purposes, the acetate

\* He prescribed also murio-sulphate.—T.

of tin obtained by means of a solution of tin (muriate) and acetate of lead.

Other (metallic) solutions are made with nitro-muriatic acid, which may be useful in dyeing. De la Folie has proposed that of bismuth; and although he begins to dissolve the metal in the nitric acid, it is however a combination with the nitro-muriatic acid, which is formed in this process by means of the muriate of soda which he adds. The solution in nitric acid alone would not answer, because, whenever it is mixed with water, the metallic oxyde falls down, forming an insoluble salt, and thereby separates without being able to unite to the colouring particles.

According to the description of this process given by Dambournay, of which he himself made much use,\* one part of bismuth is to be dissolved in four parts of nitric acid. This solution is to be poured into a bath which contains tartar, along with a solution of muriate of soda.

It has been found, that whether the solution of bismuth had been made directly with nitro-muriatic acid, or whether the solution in nitric acid was mixed with a solution of sea salt and tartar, a considerable precipitate was always formed on contact with water, although less copiously than when the simple solution in nitric acid was mixed with water. It has been remarked, moreover, that the precipitates which this solution occasioned with the decoctions of colouring substances, had an unequal colour, and speedily became brown.

#### V.—Of *Bitartrate and Binoxalate of Potash, and of Acetic Acid.*

The tartaric acid, which predominates in the bitartrate of potash, owes the properties which distinguish it from other acids, the features of which are traceable in its combinations, to its fixity and disposition to take the solid state, which is so great, that notwithstanding its affinity for water, it separates from it, and crystallizes at ordinary temperatures.

The effects of this tendency are increased by the condensation which affinity produces; while, at the same time, the action

\* Recueil de procédés et d'expériences sur les teintures solides.



which it exerts on water, as well as that of its base, is diminished by their mutual saturation.

These considerations show, that the tartaric acid might produce, with alkaline bases in themselves very soluble, combinations of little solubility, when circumstances permit them to retain an excess of the least soluble element, which is the acid. Thence arise the bitartrates, or salts with excess of tartaric acid, as also the oxalates, the bisulphates, which equally proceed from acids having more disposition to the solid state than their bases.

For the same reason, this acid produces with the bases that have little solubility insoluble salts, which have no need of an excess of acid to acquire this quality. This same insoluble combination is formed every time that combinations of acid and of bases are brought together, some of which are sparingly soluble, provided there be no excess of acid to oppose this effect by its solvent power. This disposition determines therefore the precipitates, and the exchanges of base which take place, by means of the tartaric acid, in the reciprocal action of the acids and alkalis, or of their combinations.

If in an acid and slightly soluble tartrate the proportion of base, which has of itself much solubility, be increased, proportions are attained which yield a neutral salt. Such are the tartrates of potash, soda, or ammonia, which by this increase of base have acquired a greater solubility than in the acid state, although they still possess the power of crystallizing. Should an insoluble base abstract their acid, the alkali does not part with it entirely. Thus Vauquelin observed, that on decomposing the bitartrate of potash by quicklime, which forms an insoluble tartrate of lime, the remaining alkali retained a portion of tartaric acid.

If instead of lime we make use of the carbonate of lime, it is only the excess of acid which, by its action on the lime, produces a disengagement of carbonic acid, and forms a proportional quantity of tartrate of lime. When the tartrate of potash has thereby attained the neutral state, the tartaric acid has no longer a strong enough action on the lime, to separate its carbonic acid.

Hitherto tartaric acid has not been employed in the art of

dyeing. It is the bitartrate of potash which is used. (See NOTE I.)

This salt, usually called *tartar*, is deposited on the sides of casks, from which it is afterwards detached. In its natural state it is mingled with impurities deposited at the same time. When it is separated from red wine, it retains a great deal of the colouring matter of the wine, whence it is called *red tartar*.

Tartar is purified by different processes at Montpellier and Venice. At Montpellier, the tartar is dissolved in hot water, and crystallized by cooling. The crystals are boiled in another copper, and there is added 11 or 13 pounds of the white clay of Murviel for every 22 pounds of the salt. This earth is boiled with it, and by evaporation we obtain the purified tartar, *cream of tartar*, or *bitartrate of potash*.

The process practised at Venice consists, according to the description given of it by Desmaretes,\* 1. In drying the tartar in iron boilers; 2. In bruising and dissolving it in hot water, by the cooling of which purer crystals are obtained; 3. In redissolving these crystals, and clarifying the solution with whites of eggs and wood-ashes.

In the latter process the alkali of the ashes must saturate a portion of the bitartrate: the calcareous earth must also effect a decomposition; and, towards the end of the evaporation, tartrate of potash should be obtained.

The bitartrate of potash, or cream of tartar, retains always a little calcareous tartrate.

Water dissolves less than one-hundredth of this salt at 10° Reaumur (about 55° Fahr.;) but boiling water dissolves much more of it.

Much use is made of bitartrate of potash, or tartar, in dyeing. For delicate colours it is indispensable to employ the purified salt, and it is preferable in every case. In some processes red tartar is recommended as proper to contribute by its colour to the colour that is wanted. But the red particles separate from the tartar when the salt is dissolved, and they should be regarded merely as hurtful impurities.

Of the effects produced by tartar in dyeing, a clear explanation cannot yet be given. Experience teaches merely, that it

\* Journ. de physique, 1771.

moderates the action of alum on woollens, the fibres of which are easily degraded. It is probable that the colouring particles, in fixing themselves on the stuffs, either alone or with a base, carry a small portion of it into their combination, thereby modifying the colour.

There is another salt, which has some analogy with tartar, and which may perhaps produce good effects on several occasions. This is the binoxalate of potash, or salt of sorrel, extracted from wood-sorrel in several parts of Switzerland and Germany. Scheele has shown, that the acid of this salt is the same as that obtained from sugar, and from several animal and vegetable substances, on treating them with nitric acid, whose oxygen enters into combination with a due proportion of hydrogen and carbon. But it exists native, combined in excess with potash, in wood-sorrel and some other plants. Oxalate of lime, which is insoluble, is found in several roots.

The properties which oxalic acid communicates to the different bases, and the effects which it produces on the other combinations, are to be explained, like those of the preceding acid, from its insolubility, which causes it in like manner to crystallize. Hence it is made use of in chemistry to discover the existence and the quantity of calcareous earth held in solution. But for the complete production of this effect an excess of acid must be avoided, and all its combinations must be nearly in the neutral state. The binoxalate of potash, or salt of sorrel, produces analogous effects.

This oxalate readily dissolves iron, forming a soluble salt, which renders it useful for removing spots caused by that metal. Oxalic acid produces also an oxalate of iron, which dissolves easily in an excess of acid. This property makes it be employed at present, in some manufactures, for destroying the colours whose basis is oxyde of iron.

Acetous acid, or the acid of vinegar, was distinguished from acetic acid, or radical vinegar, on a supposition that the latter contained a larger proportion of oxygen, and had thereby a greater acidity. But Adet and Darracq have shown, that between these acids there is no difference which can authorize their being distinguished. Acetic acid is merely more concentrated, and the processes by which it is prepared serve only to

exclude its water. We shall therefore designate them by the common appellation of *acetic acid*.

Acetic acid has qualities opposed, as it were, to those of the preceding acids. It is volatile, but it has a great affinity for water. \* It ought therefore to form combinations which have in general much solubility. It seems to have a small capacity of saturation; hence its combination must produce but a feeble condensation. From these causes it retains its bases but weakly, and is easily expelled from them by the action of other substances, as well as by heat. As it is volatile, and can assume the gaseous state, according to the experiments of Priestley, the action of the air promotes its separation.

This acid is formed, not only by the fermentation which is termed acid (acetous,) but also by putrefaction, as Fourcroy and Vauquelin have proved. It would appear that the substances which contain no azote are not capable of yielding this acid; for they receive no azote from the atmosphere during fermentation; and the experiments of Proust show that this acid contains a certain portion of it. (NOTE Y.)

Acetic acid is also formed in the distillation of several substances, and particularly of wood. To acid thus formed the name *pyrolignous* was given; but Fourcroy and Vauquelin have proved that it did not differ essentially from the acetic acid, and that it is merely this very acid holding in solution a bituminous oil, which is produced in the same operation, a part of which separates by keeping. It gives up the greater part of it when rectified by a second distillation. It may, however, be distinguished by the name of *pyrolignous acid*, not in order to indicate any difference of acidity, but its bituminous condition and uses.

Bosc has shown \* that this acid possessed peculiar properties for black dyes on cotton, which it derived from its carbonized oil. We shall, elsewhere, point out the interesting process, which we owe to him.

This acid merits much attention, not only for this purpose, but for several others, because it can be obtained at little expense, and its carbonized oil may be useful, or is at least not

\* Annales des arts et manufactures, tom. v.

injurious. Guyton,\* by distilling in an iron retort chips of very dry beech-wood, and rectifying the first product by a second distillation, extracted a quantity of acid, which exceeded in weight one-third of the wood employed, and the charcoal remained.

## CHAPTER II.

### *Of Alum, or the Sulphate of Alumina.*

ALUM is designated in chemistry by the name of *sulphate of alumina*; and although this denomination does not indicate rigorously the elements of which it is composed, it is however useful, and fulfils the usual purpose of nomenclature, because it denotes the ingredients which should fix attention in the greater number of the phenomena that are investigated.

This combination is of very frequent use in the art of dyeing; it is also employed in several other arts. Hence, for directing its application, we must be well acquainted with its properties and diversities; and its preparation becomes an object of considerable importance.

Alum is found in some mineral springs. It effloresces on the surface of schists in coal mines, or on the lavas in the neighbourhood of volcanoes, and on several rocks. But the greatest part of the alum employed is extracted from peculiar ores, or is fabricated by an artificial combination of alumina and sulphuric acid.

Alum is mentioned in the works of the ancients, and that from Melos in particular was esteemed among the Greeks;† but Bergmann‡ thinks that the alum of the ancients was a substance which is found native, and which differs greatly from the salt to which this name is now given; that the species of alum of which Dioscorides speaks, was rather a stalactite which might contain alum, but only in small quantity, and blended with other sulphates. In the time of Pliny,§ the best alum

\* Encyclop. method. au mot *Lignique*. † Voyage de jeune Anacharsis. tom. iv.

‡ Bergmann, de Confect. Alum. opusc. vol. i. This dissertation is of date 1767. Beckmann established the same opinion in the Mem. de Gottingen, 1778.

§ Amailhon, Mem. de l'institut, beaux arts, tom. iii.

came from Cyprus ; and its species was selected according to the colours for which it was intended. But it appears that the kind appropriated to brown colours was very impure, and contained much sulphate of iron, since Pliny distinguished it by the name *nigrum*, stating that it afforded a black colour with gall-nuts, which circumstance cannot apply to any factitious alum.

It was in the East that factitious alum began to be known. It is not ascertained at what place, or at what period it was first fabricated. One of the most ancient manufactories was that of Rhodes, a city of Syria, called at the present day Edessa. Thence comes the name of *roche alum*, which, by a confusion of words, is still given to the crystallized masses of alum. This art was carried in the 15th century into Italy, from which it was spread into Germany and the rest of Europe.

At Solfatara, near Naples, an aluminous ore is found, under the form of a white earth. The alum is formed in this ore by the action exercised on the argillaceous lavas by the sulphurous acid disengaged from the volcano by heat.

The purest alum ore is that of Tolfa, near Cevita-Vecchia. It is composed, according to Monnet, who first made its analysis, of 40 parts of sulphur, and 50 of clay, consisting of a mixture of argillaceous and siliceous earths : and besides these, a small quantity of carbonate of potash, and a very little iron. Bergmann also analyzed it, and gave nearly the same proportions. Vauquelin has still further confirmed this analysis, bestowing on it very great precision.

The other ores from which alum is extracted, are schists more or less pyritous and bituminous. Those which are too pyritous ought to be rejected, because they yield an alum which contains much sulphate or vitriol of iron, of which it would be difficult to get rid.

The operations by which alum is extracted from its ores, when it is not found ready formed in them, as at Solfatara, have for their object the alumption, the extraction of the alum, and its crystallization.

These ores, exposed to the air and the rain, may be alumed, for the most part, without being prepared ; but those which contain either too much bitumen or too much sulphur, require to be roasted before being exposed to the action of the air and

humidity; and in all, the torrefaction accelerates the formation of alum.

The *alumatation* consists in the combination of oxygen which, uniting to the sulphur, changes it into sulphuric acid, as Lavoisier has shown. But usually it is the sulphate of iron which is formed, and the iron oxydizing to a *maximum* by exposure to the air is decomposed by the alumina. There is only the mine of Tolfa, among those which are known, where the acid appears to combine immediately with the alumina. (NOTE Z.)

When the alum is formed, the ore must be lixiviated, and the liquid be afterwards evaporated till it be in a condition to yield crystals. The first crystals are to be washed, redissolved in a small quantity of boiling water, and the solution poured into peculiar casks, whose staves are then unhooped and separated, in order to get at the mass of alum which is formed.

The residuum of the crystallizations, mixed with more or less of the lixivium of the mineral, is evaporated till it be in a state to crystallize; and the process is carried on by adding the residuums of the preceding crystallizations to the new solutions.

This mixture is the principal cause of the impurity of alum, and of the differences which exist among its species.

In the progress of the chemical arts, the fabrication of alum by the direct combination of sulphuric acid and alumina has been discovered. For this purpose, a clay should be selected as free as may be from iron and calcareous earth; it must be roasted to prepare it for combining with the sulphuric acid. This combination is either made immediately with the acid, or by exposing balls of baked clay to the vapour of the sulphuric acid, in the leaden chamber in which this acid is itself manufactured. Chaptal has published the details of this process, which he established at Montpellier.\*

This mode of forming alum requires, as we shall see, an addition of potash, or sulphate of potash; and the salt obtained by this process appears to be peculiarly liable to have an excess of acid.

Before prosecuting the examination of the preparation of alum, it is proper to determine the nature of this combination.

It was at first imagined, that alum was a salt formed simply

\* Mem. de l'academie, 1788.

by the combination of sulphuric acid and alumina; whence Bergmann recommended to saturate the excess of sulphuric acid which is usually found in the lixivium of alumed earth with a pure clay, instead of the potash or putrefied urine (naturally charged with ammonia) which is commonly added. But Chaptal observed,\* that "if the acid lixivium be boiled with baked or raw clay, the solution is but slowly made, and after a long ebullition. If the lixivium be filtered, when it appears to be saturated, it lets fall, on cooling, a large proportion of the clay which it had dissolved; and if in this state the solution be concentrated, the clay separates, forming a precipitate which prevents all crystallization." From this observation we may conclude, that potash or ammonia must enter into the composition of alum. Descroizilles asserted, that the potash did not contribute to the crystallization of alum by the saturation of the acid, but by its combination; and he found, on trial, that sulphate of potash could produce the same effect. Chaptal had come to the same result, and established this practice in his factory. Lastly, Vauquelin made an exact analysis of alum, and discovered that it contained, necessarily for its crystallizing, sulphate of potash or ammonia, or both at the same time. He estimated the amount of sulphate (of potash) present in alum, drawing from his observations this inference, that whenever crystals of alum are obtained from an earthy or stony substance, by means of sulphuric acid, that substance contains potash. It has been seen, that the ore of Tolfa naturally contains carbonate of potash. Some other ores may be in the same condition. The wood-ashes formed in their roasting, supply them likewise with potash and sulphate of potash. Hence it is not surprising that alum may be obtained without the addition of potash, or putrefied urine, to furnish the ammonia. Bergmann remarks, that the latter addition gives rise to an alum which alters the colours. It is not known whether it be by too large a proportion of sulphate of ammonia, or by the mixture of some other hurtful substance, that alum may acquire this bad quality.

It may be remarked, that Bergmann had himself discovered,† after his first work, not only that it was not for the absorption

\* Mem. de l'academie, 1788.

† De platina. § Opusc. vol. ii.



of the excess of acid that potash or ammonia was necessary to the formation of alum, but that they were still efficacious when in the state of sulphate.

It ought not, however, to be thence concluded, that the effect is entirely the same, whether potash be employed, or sulphate of potash. By the first, the requisite saturation of the acid, when it is in excess, is greater, and consequently the production of alum ought to be more considerable, if enough of alumina be present. Whenever, therefore, there is an excess of acid, but a defect of potash or alumina, the advice of Bergmann may probably be followed with advantage, namely, to add alumina, and at the same time a sufficient quantity of potash. To accomplish this twofold object we may employ, as Vauquelin points out, the residuum of the distillation of nitrate of potash by clay, which may be particularly adapted to the fabrication of alum by means of sulphuric acid.

In the prices of the alums of commerce there is a considerable difference, and that of Rome is generally preferred for colours that are to be lively and clear. By analysis, therefore, must be discovered what are the differences which distinguish alums from one another.

Vauquelin has brought to the analysis of alum the precision and accuracy which characterize his researches.\* On decomposing alum by potash, its ammonia is disengaged. On the other hand, by decomposition with ammonia, evaporation of the liquid, and drying the residuum strongly, the sulphate of potash is obtained by itself. By this means Vauquelin has ascertained that alum contains nearly 7 per cent. of the sulphate of potash or of ammonia; and this quantity is usually divided between both of these sulphates. (NOTE AA.)

He has recently examined five kinds of alum taken from different factories. He determined the proportion of acid which each contained, by precipitating the sulphuric acid with barytes, and comparing the weights of the precipitates. He had previously precipitated the alumina by ammonia, and subjected it to a strong desiccation.

It results from his experiments, that these five kinds of alum, among which was the alum of Rome, afforded proportions almost

\* Ann. de chimie, tom. xxii.

rigorously the same; and that the quantity of iron which is found, for example, in that of Liege, of good quality, is nearly the same as what he obtained from Roman alum. Hence he is led to believe, that it is only from a prejudice that the last continues to be preferred; and if a proportion of iron which can do harm be present, he recommends to get rid of it by prussiate of potash.

We shall deviate a little from the consequences to which the experiments of this great analyst seem to lead. 1. We have examined alums, particularly artificial ones, which contained undoubtedly a pretty considerable excess of acid, for they left, after their crystallization, a very acid liquor. What Vauquelin has found in the five specimens, four of which had been sent by the manufacturers themselves, and were consequently choice samples, does not authorize the conclusion, that all the alums in the market have a like proportion of acid.

2. We have mixed with a solution of the alum of Liege, which appeared to be very pure, a little gallic acid; and a similar test was applied to the Roman alum. The first assumed a black hue, and the second did not change. Analysis would probably have pointed out but a slight difference; but this slight difference is sufficient to produce an alteration on lively colours, for which, especially, a severe choice is requisite.

After submitting this alum to crystallization, in which the first formed crystals were taken, the solution of these crystals was no longer effected by the gallic acid, so that it then presented properties completely analogous to those of Roman alum. Bergmann had already observed this effect of a careful crystallization, which he recommended.

With regard to the iron present in alum, and which may exist in considerable proportion when it is crystallized with little care, Monnet had formerly observed, that the sulphate of iron could be entirely separated by crystallization; on the other hand, Leblanc has made mixed crystals of sulphate of iron and sulphate of alumina, (*sulfate d'alum.*) These facts would seem to be reconcileable, by the consideration of the state in which the iron exists. When highly oxydized, as it undoubtedly is in the lixivium of alum ore, it requires a great excess of acid to be susceptible of solution, and the oxyde must precipitate, as we shall afterwards see, during the evaporation

and crystallization, or be retained in the uncrystallizable residuum. But if a little oxydized sulphate be mixed with the sulphate of alumina, and if crystallization take place immediately, the iron no longer requires in this case an excess of acid. It may thus be placed in circumstances which allow it to form a combination.

To recapitulate: We conceive that, in the manufacture of alum, matters should be so managed as to leave no excess of acid, and to avoid those additions of uncrystallizable residuums, which it is proper to treat separately, according to Bergmann's advice, whether it be for extracting their salts, or for making an alum out of them, which afterwards requires more care for its purification, or an alum intended for purposes where it is not needed to be pure. In the second place—The crystallization should be so conducted that the purity of the salt shall not be affected. Consequently, it should not be suffered to condense in great masses, but have a residuary liquid that may retain what would affect the qualities required in the combination. To accomplish this object, the crystallizations might be reiterated, and all the residua treated separately.

It appears to us that this art is improving progressively, as the manufacturers are becoming more enlightened in the conduct of their operations, and that there will soon be no need of having recourse to Roman alum.

Those who require alum need not make a selection in employing it for sombre hues; but they should be very nice with regard to lively and clear colours. Instead of analysis, which requires time and practised skill, we propose to them, 1. To crystallize a portion of the alum which they are to use; if the residuum be perceptibly more acid, this alum might modify the colours by its excess of acid: 2. To mix a little of the infusion of gall-nuts with the solution of alum; although, by its own colour, this infusion may be less proper for this trial than pure gallic acid, it will point out sufficiently well if the alum contains an injurious quantity of iron. In this case, the alum may be purified by one crystallization, leaving sufficient (liquid) residuum.

When an exact analysis of alum is wished to be made, we must not lose sight of the difference which, according to the means employed, exists in the insoluble precipitate, from which the proportion of alumina is to be determined.

If the precipitate be made by means of a carbonate, it retains a considerable proportion of the acid, and even of the alkaline base; for on dissolving it in nitric or muriatic acid, alum is obtained by crystallization. The best agent is ammonia; but it is difficult to deprive this precipitate sufficiently of sulphuric acid, so as not to produce a precipitate of sulphate of barytes, when its solution in nitric or muriatic acid is mixed with a solution of a barytic salt.

Another circumstance impairs the precision of these comparative determinations. When the solution of alum is very dilute the alumina retains water, which it does not give entirely up at a very strong heat; but when it is concentrated, the precipitate which it affords abandons the water much more easily, according to the observation of T. de Saussure.\* Hence, from the circumstances of the precipitation, and the degree of heat at which the precipitate is dried, there may exist great differences in its valuation.

According to Bergmann, 100 parts of sulphate of alumina (alum) contain 18 parts of alumina. T. de Saussure reduces this quantity to 0.09, and Vauquelin, in his last analysis, to 0.085.

Lime and the alkalies, mixed in certain proportions with the solution of alum, cause this salt to take a cubical form. Sieffert appears to have first described this variety of alum.† Leblanc has made interesting observations on the crystallization of this salt, not yet analyzed by chemists. It must have the acid properties in a less degree than ordinary alum, as Vauquelin thinks, and it would appear, that from the stronger action of the alkaline base on the acid, this salt would give up the alumina more readily to the colouring particles, since alkali is commonly added to the solution of alum for precipitating their lakes.

According to Bergmann, 30 parts of water are required for dissolving one of alum; 3 parts of hot water are sufficient.

We have remarked, that in several woollen dyes tartar was added, which had the property of moderating the action of alum on the filaments, without attempting to explain how it impaired

\* Journ. de Phys. tom. lli.

† Sieffert's *Versuche mit einheimischen Farbe Materien*, &c., 1775. Sieffert quotes a dissertation on cubical alum, which he printed in the "Edinburgh Magazine." For obtaining this alum, he prescribes the mixture of 12 parts of alum with one of quicklime slaked in the atmosphere, dissolving this mixture in boiling water, and evaporating gently.

its energy. Bancroft observes, that the dyers indeed frequently omit the tartar, diminishing at the same time the usual proportion of alum.

Linen and cotton have less disposition to combine with alumina than animal substances. Hence, a small proportion of soda or potash is commonly added, which must favour, as has been said, the decomposition of the alum.

This method is not sufficient for qualifying alum to become a mordant on printed goods. The solution which contains the alumina must be concentrated, without having crystals formed in it. The acetate of alumina has not only this advantage, but it possesses likewise another, dependent on the acetic acid, which serves as the solvent. This acid acts only by a weak affinity, and consequently retains the alumina more feebly than the sulphuric acid; and in the drying, to which goods impregnated with the mordant are subjected, its volatility makes it fly off, so that these goods do not carry into the bath an acid which might injure the colour. These advantages render the acetate of alumina a very fit substitute for the ordinary aluming in several cotton dyes, accommodated to the improved process of calico printing; but acetic acid scarcely effects a solution of alumina, as it exists in clays. Their force of cohesion is too great an obstacle for the weakness of the acid to overcome. It is by means of the acetate of lead that an exchange of bases is produced, which we shall have occasion to examine. Hence the preparation of acetate of alumina amounts to a price which does not permit its use in several dyes, till a mode be got of preparing this combination less expensively. The properties of acetate of alumina led us to believe, that it might be substituted with success for alum in the dyeing of wool. We have made trials with madder; but the cloth took a less intense colour, without our being able to point out the cause of this result, dependent probably on some circumstance which we overlooked. (See NOTE D.)

Alumina dissolves pretty copiously in potash and soda, especially by calcination. Macquer was much occupied with this solution, in order to employ it in dyeing. But as the alkalies possess the property of dissolving colouring substances, and of abstracting them from the stuffs on which they are fixed, they

do not seem fit to serve as solvents of alumina. The experiments of Haussmann, however, prove that this mordant may be employed in some circumstances with advantage. (NOTE BB.)

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### CHAPTER III.

#### *Of the Sulphate and some other combinations of Iron:*

THE sulphate, or *vitriol of iron, martial vitriol, green copperas*, is not a uniform and identical combination. It varies, not only by the admixtures which may be present, but also by the state of the oxyde of iron, whence very different effects may result from its action.

The sulphate of iron may be directly made from iron and sulphuric acid diluted with a certain quantity of water; and a combination may thereby be obtained, possessing determinate qualities. But the low price of this article rarely allows of this manufacture being conjoined with that of sulphuric acid.

Sulphate of iron is found native in coal-mines, in the cavities of pyritous mines, and in schists. But the most part of what is employed comes from the martial pyrites, or natural sulphurets of iron.

These substances are composed of iron, sulphur, alumina, siliceous earth, and sometimes calcareous earth, in different proportions. The formation of the sulphate of iron in these minerals is effected by exposing them for a long time to the action of air and moisture, or by roasting them in the open air, and leaving them afterwards exposed to its action. This operation must sometimes be reiterated. The sulphate that is formed is extracted by lixiviation and evaporation.

The iron in the native sulphurets of pyrites is oxydized, for when they are exposed to the action of fire in a retort, sulphurous acid is evolved, which does not happen with the sulphurets with the metal. It is de-oxydized in this operation, and the residuum is a pure sulphuret.

Sulphate of iron is also formed in the mineral waters which hold copper in solution, after it is precipitated by iron. This solution, which retains a little copper, is thereafter crystallized.

The sulphate of iron of Goslar contains commonly a little

zinc, and that of Hungary and Saxony a little copper.\* The sulphates of England and France are purer. They contain, however, sometimes alum, especially those of France.

Sulphates free from copper or alum would be formed, if the precaution were taken of keeping fragments of iron in the boiler, which serves for evaporation, as Monnet recommends;† for iron slightly oxydized has the property of precipitating copper and the base of alum. The superiority of English vitriol seems to be owing to this precaution. The same practice is also observed in two manufactories in the neighbourhood of Alais.‡ The zinc alone would not be precipitated. But it is rarely found, and only in small quantity, in the sulphates of iron.

The copper which exists in several kinds of sulphate of iron is not injurious to the black dyes, in which this metallic salt is principally employed; but for other purposes, it must be got rid of. This is easily effected, by keeping for some hours in a cold solution of this salt, plates of iron, on which the copper precipitates. But this operation could not be performed by crystallization, because, according to the observation of Monnet, the sulphate of iron and that of copper form a compound salt that cannot be thus separated.

Alum is probably more injurious to black than copper is; for when a black stuff is boiled with alum, it destroys the colour by dissolving it.

The sulphate of iron varies in its properties according to its state of oxydation.

It is almost colourless when its metal is very slightly oxydized, or in the condition of black oxyde. It assumes a red colour when the iron is much oxydized, constituting a red oxyde. Proust, who directed our attention particularly to the two states of iron, and to their distinctive properties, regards them as two fixed terms of oxydation, between which there is nothing intermediate. We cannot adopt, in this respect, the opinion of this chemist, whose delicate and numerous observations have contributed so much to the advancement of the science. As the causes, however, which may produce the oxydation or de-oxydation of this iron, make it usually pass from a very advanced

\* Mineralogy of Kirwan.

† Traité de la vitriolisation.

‡ Elémens de chimie de Chaptal, tom. iii.

degree of oxydation to another adjoining the lowest degree, we neglect this consideration, and conform usually in our explanations with the opinion of Proust. (NOTE CC.)

When the solution of slightly oxydized iron is exposed to the air, it becomes gradually turbid, and lets fall a yellow precipitate. If the effect be complete, crystals are no longer obtainable by evaporation, but an extract is got, which has a great excess of acid. Highly oxydized iron then requires an excess of acid for its solution; and when it is in this state, the sulphuric acid has much difficulty to dissolve a smaller quantity of it, than if it is in the metallic form. By the decomposition of water which occurs in the latter case, it can take only the state of black oxyde. If the crystals of the sulphate of iron be left exposed to the air, they lose their green colour, becoming dull and yellowish. Their solution now yields only a salt with excess of acid, and an insoluble yellow substance remains. It is obvious, therefore, that in order to preserve the sulphate of iron or its solution in its primitive state, air must be excluded.

The precipitate now spoken of, is a salt with excess of oxyde. By means of an alkali, the acid may be abstracted, when merely a red oxyde remains.

If iron be put into a solution of the highly oxydized sulphate, a yellow precipitate is deposited, which is also a salt with excess of oxyde, and the solution resumes the state of green sulphate. Hence appears the utility of adding iron in the preparation of the sulphate. It is thus obtained in the state for forming crystals, and those uncrystallizable residuums called *mother waters* are avoided.

The sulphate which contains the black oxyde is in a much greater state of saturation, and we have seen that gallic acid could not separate and precipitate this oxyde from the sulphuric acid. It is not to be doubted, then, that it exerts a far more energetic action on the acid, than when it is much oxydized.

In the precipitates produced by the alkalies, from the solutions of both sulphates, characters appear which depend on this difference of action. The little oxydized sulphate affords with the alkalies greenish precipitates, which retain a greater proportion of acid in like circumstances; and even when the sulphate is highly oxydized, its precipitates are red, and do not retain any acid. If we treat with a concentrated alkali the



green precipitate obtained from the slightly oxydized sulphate, its acid is removed, and it becomes grey or black. On exposing it to the air, it continues to oxydize, passing to yellow. It then grows red, by the action of an alkali which seizes its acid.

What we have now advanced concerning the difference which distinguishes the green sulphate from the red sulphate, must be applied to all the solutions of iron in the acids. The whole of them form a more intimate combination with the black oxyde than with the red. They exhibit, besides, differences dependent on the energy of the acid. Thus, muriatic acid dissolves highly oxydized iron more easily than the other acids. It is true, that if it contains an excess of oxygen, a portion of the acid forms chlorine, according to the observation of Fourcroy. Iron produces also in the precipitation of highly oxydized muriate, a yellow precipitate, which owes this colour to the acid remaining combined with it. But it may be supposed, that highly oxydized muriate of iron would be less proper for black dyes than the sulphate, because it would retain with more force the oxyde which must enter into the formation of the black molecules.

Acetate of iron is employed for printed calicoes, and in general for black colours in linen and cotton, for the same reasons which make acetate of alumina be preferred. But we need not have recourse to so costly a process. Acetic acid dissolves iron directly; and to have it in the most oxydized state, fragments of the metal must be kept a long time in good vinegar. The object would not, however, be accomplished, were the solution left always over the iron. For we have seen, that in the metallic state it precipitates a highly oxydized salt. The liquor, then, is to be decanted, and kept in a vessel where it may have contact of air, so as to pass to the highly oxydized state. This decantation ought to be made whenever the solution is completed.

For the ordinary black dyes, where there is no need of so concentrated a solution, vinegar is not employed, but a less expensive acid is frequently formed with different vegetable substances, for example, with the bark of the birch tree. To the vessel in which this operation is executed, the name of *tonne au noir* (black cask) is given. This object would be

better accomplished, if the precaution were taken to keep the solution, after it is made, out of contact of iron. (NOTE DD.)

In explaining the action of astringents, we have mentioned the observation of Proust, who found that the highly oxydized sulphate was brought back to the state of the little oxydized, by the action of astringents, and even of other colouring substances; whence he concludes, that it is right to employ in dyeing only the highly oxydized sulphate. This conclusion appears to us just, when black dyes are in question, with the exception, perhaps, of the dyeing of silk. It should even be applied to all solutions of iron used for this purpose. But the same thing does not hold true when solutions of iron are made use of for other colours. For example, in the manufacture of printed goods, in order to obtain the colour called *rust yellow*, sulphate of iron is made use of, or, still better, the little oxydized acetate, formed by the decomposition of acetate of lead with sulphate of iron. The salt with excess of oxyde, which is formed in the cloth, has an agreeable yellow colour, which, by the contact of alkalies, passes to grey; after oxydizing in the air, it becomes red.

The shades of yellow which may be given to cotton by means of iron, with which we shall be elsewhere occupied, prove that it is not the oxyde of iron alone which serves to give colour in this instance, but that the precipitate retains a portion of the acid; for it is always to an acid that the oxyde of iron owes this colour.

The changes of colour must never be lost sight of, which result from the different oxydations of iron in the dyes, where it is used for other colours besides black, as Chaptal has shown. Thence the precautions which must be taken, in order that this oxydation shall go on uniformly during the operation itself, and that the stuff be exposed to it in an uniform manner.

There is one operation for which the iron should be, on the contrary, at the lowest stage of oxydation: this is the solution of indigo, by means of the sulphate of iron, precipitated by an alkali. Slightly oxydized iron gives solubility to the indigo, by carrying off the oxygen, which renders it insoluble. The oxyde of copper produces a contrary effect, affording oxygen to indigo deprived of it. This renders the sulphate and acetate

of copper proper for the *reserves*, that is to say, for preserving the parts of the cloths to which they are applied, from the fixation of the indigo, which by resuming oxygen, can no longer combine with the stuff.

The differences of oxydation of the metallic substances employed in dyeing, and the effects flowing from them, merit the greatest attention; and by observing them with more care than has hitherto been done, several operations will be rendered methodical (*regularisées*), whose results are regarded as capricious, becoming at the same time more uniform and more advantageous.

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## CHAPTER IV.

### *Of Sulphate of Copper.*

THE sulphate of copper, *blue vitriol*, *vitriol of Cyprus*, *blue copperas*, is not much employed in dyeing; but it is of great service for forming the colours used, particularly for painted papers; and hence its fabrication, and the means of obtaining it pure, have become interesting to the arts.

Different methods are employed for making sulphate of copper. The native sulphuret, or copper *pyrites*, or *mate*, resulting from the fusion of copper ore, which is a combination of copper and sulphur, is calcined, and the product of the calcination is left to effloresce. The copper thus deprived of a portion of its sulphur oxydizes, and the sulphur is converted into sulphuric acid. The salt that forms is then extracted, and crystallized. A second process, analogous to the preceding, consists in calcining a mixture of copper and sulphur, in exposing the sulphuret in like manner to effloresce, lixiviating the salt, and crystallizing it.

Since the (modern) fabrication of sulphuric acid has allowed it to be employed for several purposes to which its former price was an obstacle, sulphate of copper has been formed, by dissolving the metal, or its oxyde, in sulphuric acid. To this sulphate it is objected, that for some purposes it contains an excess of acid; but it would be difficult to avoid this inconvenience.

There are some native waters which contain sulphate of copper.

The principles to be attended to in purifying the sulphate of copper deserve to fix our attention, because they are applicable to all the metallic solutions, and may explain several phenomena observed in the chemical action of different bodies.

The insolubility of any compound that is formed, should be considered as a cause of its formation, whenever the elements that can produce it are brought together. Thence may be deduced, as we have said, the cause of the precipitations and changes of base, which occur in the reciprocal action of the acid and alkaline substances.

The same effect takes place in the reciprocal action of metallic oxydes and acids. The oxydes can seldom produce neutralization in combining with the acids, when their combination retains solubility; but these combinations require a greater or less excess of acid, a condition which varies according to the state of oxydation. Thus we have seen, that the highly oxydized sulphate of iron requires a considerable excess of acid, which the lowly oxydized sulphate does not. If the excess of acid be removed, the highly oxydized salt, which is insoluble, precipitates.

It thence results, that when a metal is in solution, and when it needs an excess of acid in order to preserve this state, the addition of another oxyde, which shall require a less considerable excess of acid, will cause the first to fall down in the form of an insoluble salt; and if the second needs an excess of acid, although less considerable, it will be precipitated in its turn by an oxyde which is soluble without excess of acid, or which requires less of it.

For the same reason, different effects will be obtained, by varying the oxydation of a metal, and thereby the solubility of its combinations. Thus we have seen, that iron precipitated the highly oxydized sulphate, forming a combination which preserves its solubility without excess of acid. In these circumstances two combinations are produced, one which remains in solution, and another which is insoluble. The action even of the alkalies is usually limited to the production of a similar effect on metallic solutions.

Gay Lussac, who established this point of theory,\* supported

\* *Annales de chimie*, tom. xlix.

it by several interesting facts. We shall confine ourselves to an account of the observations which relate to the preparation of the sulphate of copper and the sulphate of iron.

“When the iron is highly oxydized, it is precipitated by the oxyde of copper; when slightly so, the reverse takes place. Here are two consequences of great importance, because they are susceptible of frequent applications to the arts: the first is, that the whole iron can be separated from a solution of copper; the second, that the whole copper in a green solution of iron may be removed.

“Several colours are prepared with the sulphate of copper, but the iron which it always contains, and which has not hitherto been completely separated, alters their shade. If, for accomplishing this object, the iron be strongly oxydized by means of nitric acid, or still better, by chlorine, it will be precipitated entirely from the sulphate of copper, by pouring into it a sufficient quantity of potash, heating and agitating the liquor very well.

“The green sulphate of iron is pretty frequently employed in the arts, and in several cases it is of consequence to free it from all the copper. Iron has indeed the property of separating it, but it appears to do so but very imperfectly, and in a long time. It will be undoubtedly more advantageous to employ potash, pouring a little of it into the green sulphate. The precipitate of black oxyde of iron will soon return into solution by agitation; and it will throw down at once the oxyde of copper, and the red oxyde of iron, if either exist in the green sulphate.”

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## CHAPTER V.

### *Of Verdigris, or the Acetate of Copper.*

FORMERLY verdigris was prepared only in Montpellier and its neighbourhood. The process followed there consisted in causing the stalks of grapes to ferment along with the *vinasse* (wine-lees), then plates of copper were arranged layer upon layer with these stalks, and the whole was left together for some time. On withdrawing the plates, they were set aside in a corner of the cellar, where they were further sprinkled with

wine-lees; and lastly, the verdigris formed by this operation was scraped off.

This process has been improved and rendered more economical in these latter times, by substituting for the stalks the squeezed husks of grapes, previously subjected to the acetous fermentation, thus suppressing the vinous matter with which they had formerly bedewed the stalks. Chaptal has described the details of this process.\*

At Grenoble, ready-made vinegar is employed, with which the plates of copper are moistened. The verdigris prepared in these two methods differs in some of its properties.

Chaptal has made a comparison of them.† The first is unctuous, pasty, little soluble in water; it is preferred for the purposes of painting. The second is drier, of a more decided greenish blue colour, and more soluble in water. It produces better effects in dyeing; giving more vivacity to the colours, and requiring a smaller quantity to compose the mordants.

This difference depends upon their composition. The first contains, in particular, uncombined oxyde of copper, or carbonate of copper, and the second approaches to the state of an acetate.

In either preparation of verdigris the copper is reduced to an oxyde by the concurrent actions of atmospheric air, and the acetic acid employed or formed. But as copper vessels are much used, it will be proper to dilate a little further on the manner in which the acids act on this metal.

For dissolving copper in the acids, it must, like other metals, be combined with oxygen or reduced to an oxyde. Hence it must either attract oxygen from the atmosphere, or obtain it from the acids, or from the decomposition of water by the co-operation of another force; for it has not this property of itself.

The vegetable acids cannot yield oxygen to copper; but the action which they exercise upon it so favours its combination with oxygen, that it attracts it speedily from the atmospheric air, and is reduced to an oxyde so as to become soluble in the acid liquid. This must not be hot, in order that the copper may attract oxygen from the atmosphere. The vegetable acids do not attack copper while they are hot, and the same thing takes place with oils and other substances which act on this

\* Mem. de l'instit. vol. ii.

† Mem. de l'instit. vol. i.

metal, unless there be a portion of copper already oxydized; for in this case it dissolves readily, whatever temperature the liquor may have. Hence we perceive the necessity of never allowing liquors that can corrode this metal to cool in copper boilers, and of taking care to keep them always very clean, so that no oxyde is formed on their surface.

Nitric and nitro-muriatic acids, though diluted with water, afford oxygen to copper, especially at a boiling heat. Hence they must dissolve a portion of this metal in the baths into which, for example, solution of tin enters, unless the boiler be tinned with care. This effect may be diminished, however, in consequence of the nitric acid exerting its action on the vegetable, and more particularly the animal substances present in the bath, and from its being saturated by the ammonia that is generated.

In verdigris, copper is reduced to the state of oxyde, and is combined with a more or less considerable proportion of acetic acid. When the oxyde is completely saturated with this acid, it is wholly soluble in water, and forms by evaporation rhomboidal crystals of a blue colour, which attaching themselves to little wooden rods, give origin to those groups called crystalized verdigris, or crystals of Venus. There is this difference, then, between this salt and verdigris, that in the first the oxyde of copper is completely saturated with acetic acid, forming an acetate of copper; while, in verdigris, there is but a variable proportion of the oxyde of copper in the condition of an acetate. This saline portion can be separated by solution in water. There remains, in this case, only an oxyde of copper, or a salt with excess of oxyde, which dissolves readily in acetic acid, and thus is converted to the saline state. Sometimes the verdigris contains but very little acetate; sometimes, on the contrary, it contains scarcely one-fourth of its weight of oxyde of copper uncombined; in which circumstances consists, as we have said, the difference which distinguishes the verdigris manufactured at Grenoble from that of Montpellier. (NOTE EE.)

Clegg, in attempting to substitute for verdigris in the black dye an ingredient less expensive, says, that he observed that the copper of verdigris threw down, in the state of an oxyde, the iron of the sulphate of iron held in solution along with astringent matters. Regarding verdigris, therefore, as a pre-

cipitant of iron, he sought to substitute for it other substances capable of precipitating this metal from its solvents. He first tried the alkalies; and his experiments, which on the small scale appeared to succeed, had no success on the great. In fact, the alkalies do not precipitate the combination of iron and the astringent principle: but they unite along with it, giving it a reddish hue. He next ascertained, by several trials, that the verdigris might be perfectly replaced by a mixture of sulphate of copper and potash. He prescribed the dissolving the sulphate of copper, and adding to it solution of potash, till the blue colour disappeared, that is to say, till the whole of the copper was thrown down. For this purpose a nearly equal weight of sulphate of copper and of alkali is required. He asserts, that the weight of the two together is a substitute for an equal weight of verdigris; and that this process may be put in practice, especially for hats, the dyeing of which consumes a great deal of verdigris.

We shall remark on this process, that the oxyde of copper produces in reality a precipitate in a solution of iron blackened by an astringent; but this precipitate is not solely oxyde of iron; it is owing to the black molecules which result from the combination of the oxyde with the astringent principle. This precipitation, may, indeed be one mode in which oxyde of copper contributes to dyeing of black; but it is probable that the principal way in which it is useful to this dye consists in forming a blue with logwood, which also enters into it, or a shade between green and black, which results from its combination with the astringent; for we have observed, that it was advantageous for deepening the black to derive it from different colours. It is thus obvious how a verdigris which contains much acetate of copper may produce better effects than one which has a larger proportion of unsaturated oxyde, or carbonate.



## CHAPTER VI.

*Of the Acetate of Lead, or Salt of Saturn.*

THE acetate of lead is a combination of lead reduced to oxyde, and of acetic acid. It is usually crystallized in slender confused needles.

This salt has a sweet taste, mixed with a little astringency, which has caused it to get the improper name of *sugar of saturn*.

Acetic acid out of contact of air does not attack lead in the metallic state. But if the air touches its surface, the lead is gradually oxydized by means of the oxygen which it attracts, and thereby becomes soluble in the acid. As this manner of preparing the acetate of lead would be disadvantageous, both because it would take much time, and a large portion of the acid would evaporate, other processes are had recourse to.

White lead is an oxyde of lead combined with carbonic acid. To form it, the metal in plates is suspended over vinegar in earthen vessels, which are covered with horse dung, to afford heat for evaporating the vinegar, which exhaling, reduces the lead to an oxyde by means of the air, and then dissolves it. Carbonic acid is evolved at the same time, which precipitates the lead as carbonate. This carbonate, pulverized with much care, constitutes white lead. But a portion of the oxyde is retained by the vinegar, forming acetate of lead, which is merely to be evaporated and purified by a second crystallization.

The greater part of the acetate of lead is prepared with distilled vinegar, obtained from beer or wine, and with white lead, which being reduced to a very subtile powder, is in the most favourable state for dissolving.

If no acetate of lead be at hand, it is easy to manufacture it one's self, by dissolving an oxyde of lead in distilled vinegar, and evaporating the solution to the proper point of crystallization. Different oxydes of lead may be employed. White lead dissolves more easily than the others, except ceruse; but we must avoid the latter, because it is a mixture of white lead and chalk. Litharge, or semi-vitrified oxyde of lead, may be substituted for white lead; minium dissolves with more difficulty.

It would probably be sufficient to dissolve the oxyde of lead

in white (pale) vinegar, whose extractive part, by which principally it differs from distilled vinegar, would do no harm; but it must be remarked, that the acetate of lead is a compound not uniform in its proportions. Thenard has observed, that the ordinary acetate of lead can still dissolve a quantity of oxyde almost equal to what it already contains, and then it assumes a different form of crystallization. But the new crystals are decomposed by simple exposure to air, and a portion of the oxyde is converted into carbonate. On being dissolved in water, they likewise abandon a portion of the oxyde, forming an abundant precipitate; after which the soluble combination is restored to the ordinary state.

On repeating this experiment, we have observed that the acetate of lead which we used, reddened the vegetable colours, acting on paper stained with turmeric like feeble acids; but after being surcharged with oxyde of lead, its solution reddened the tincture of turmeric like alkalies, so that there is here an indication of the alkaline properties which the oxydes exercise on the acids.

The crystals of acetate of lead usually afford a slight precipitate when they are dissolved in distilled water; which precipitate is owing to carbonate of lead formed at their surface. But they produce, with the waters of rivers and wells, a much more abundant precipitate, arising from the sulphates and the muriates which are present in these waters, the quantity of which is proportional to that of these salts. The chloride of lead, however, has a certain degree of solubility.

The acetate of lead is not employed directly as a mordant in dyeing, although it produces an abundant precipitate with the greater number of the solutions of colouring matters; but its precipitates have sombre and dead hues. The chief use that is made of it, is to procure acetate of alumina. Since the force of cohesion of this earth is opposed to its direct solution in the acetic acid, a mixture of sulphate of alumina is made with acetate of lead. Thus (acetate of) alumina is procured in the liquid state. But the elements of these combinations being placed together, and the oxyde of lead possessing the property of affording an insoluble combination with sulphuric acid, this compound is formed and precipitates, while the alumina remains dissolved in the acetic acid. (See NOTE D.)

Accident made known this combination, so important in the

printing of calicoes; several useless substances indeed were added to it, till chemistry determined the essential ingredients.

Certain expert manufacturers imagined, that they should preserve among the ingredients a given proportion of chalk and potash, with the view of absorbing an excess of acid; but this addition does nothing but throw down, uselessly, a portion of the oxyde of lead, and introduce into the acetate of alumina foreign salts, which may injure the effects that it ought to produce. Experience has proved, that without these mixtures a good preparation was obtained; hence the only thing to be determined is, the proportions which effect the exchange of base most completely. (NOTE D.)

Haussman employed an acetate of tin, formed by decomposing the acetate of lead by the muriate of tin; but this preparation has some disadvantages:—1. It retains a little chloride of lead; for this salt has a slight solubility. 2. A triple salt is formed, which contains a great proportion of lead, if the necessary proportion of acetate of lead be used.

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## CHAPTER VII.

### *Of the Fixed Alkalies.*

MAGNESIA, lime, barytes, strontian, and glucina, might indeed be regarded as fixed alkalies, since the whole of them, and some more than potash or soda, possess the property of saturating the acids, and forming with them neutral combinations. They are distinguished, however, by the name of earths, or alkaline earths, in consideration of the solidity and pulverulency which give the idea of an earth; and the name of fixed alkalies is reserved for potash and soda, which being of great use in dyeing, should be well studied.

As for ammonia, although it be the most powerful of the alkalies, since, in equal quantity, it exercises in a higher degree the alkaline properties on the acids, its volatility is an obstacle to its use in most part of the operations of dyeing.

#### I.—*Of Potash.*

Potash, named *vegetable alkali*, because it is derived from

the combustion of vegetables, is an identical substance. But the state of saturation in which it exists, and the mixtures confounded with it, considerably diversify its effects and value.

When its whole alkaline power is to be exerted, it must be deprived of the carbonic acid, with which it is combined in greater or less proportion, and which gives it the property of effervescing with such acids as expel its carbonic acid. With this view it is dissolved and treated with quicklime, which, seizing its carbonic acid, precipitates in the form of an insoluble salt. What is called pure or caustic potash, is thus obtained. It still retains, however, a portion of carbonic acid, to free it from which it must be treated with alcohol. In this case two combinations are formed, the one an *alcohol* (alcoate) of potash, and the other, which remains dissolved in a portion of water, or which separates in crystals, is carbonate of potash. On expelling the alcohol from the former combination, we have pure potash. But this preparation is not wanted in dyeing, except for experiments of research.

The watery solution of ordinary potash contains also foreign salts, which it may be worth while to separate, as is done for the manufacture of fine glass. For this purpose, the potash is dissolved in as little water as possible, and the solution is allowed to settle. The salts less soluble than potash, separate in a great measure, and fall down.

Potash, not saturated with carbonic acid, attracts the humidity of the air, and thereby dissolves, forming a liquor called *oil of tartar, per deliquium*. It also attracts carbonic acid, and in a long period of time acquires the property of crystallizing. Bohn and Monnet had observed this crystallization before its cause was known.

It should be observed, that carbonate of potash has the property of crystallizing, before getting the quantity of carbonic acid which can combine with it. When this is the case, it attracts moisture from the air. In the solution, the portion which remains liquid, acts sufficiently on the water to permit the other portion to crystallize. When this water is removed, the crystals exert sufficient force on the water of the atmosphere, and attract enough to be reduced to a liquid. It would seem, that the carbonate of potash can assume variable quantities

of carbonic acid, even when it has no longer the property of attracting humidity.

These different states of saturation of the carbonic acid demand attention, when potash is employed in dyes whose colours may be affected by it; or in which the texture of the stuffs can suffer alterations; for, in the caustic state, the alkali exerts a greater power of combination with other substances.

Different names have been given to potash, according to the substance from which it is extracted. It is called *salt of tartar*, when obtained from the bitartrate of potash, or tartar. To make this preparation, the tartar is wrapped up in paper cones, and is thus exposed to combustion. After dissolving the residuum in water, the solution is concentrated by heat, the foreign salts are separated in proportion as they fall down, and by desiccation the potash is procured, which retains much carbonic acid, formed by the destruction of the tartaric acid, at a sufficiently moderate heat for a great deal of it to remain in combination. This potash is very rich in alkali; but it is very costly.

The *cendres gravelées*, which are the product of the combustion of wine lees and vine branches, are also rich in alkali, although the potash is here less pure than that obtained from tartar.

The potash, known by different names in commerce, comes chiefly from the North of Europe, and the United States of America. It is the product of combustion in vast forests, for the wood of which no better use can be found. But this operation not being every where made with the same care, is the main cause of the great differences in the product. According to Linnæus, the birch or alder is burned with a slow fire; with the ashes and water a kind of paste is made; with this paste a range of billets of the pine or fir is covered; over this range another is laid transversely, covered in like manner with the same paste; and in this manner the layers of wood and paste are continued, till the pile acquires a considerable height. Fire is now put to it, and when the ashes begin to flow, the pile is overturned, and the ashes in semifusion are beat with flexible rods. They are incrustated by this operation on the logs, and become as hard as stone.

It is obvious, that by this process the potash must contain a

great deal of foreign earth; but it appears that lime is sometimes mixed with it. Home found some of it, chiefly in a species of potash called *cassoude*, much used by the bleachers in Belgium, and the neighbouring departments.

So defective a process as the above is not followed every where; but in some places the ashes are lixiviated, by covering them with water in casks. After some hours, the liquid is run off, new water is poured on, and the operation is repeated, till the water comes off nearly insipid. The last waters are employed for new leys, as in the *lixivia* of the plaster rubbish from which saltpetre is extracted. The waters are subsequently evaporated; the result is black and carbonaceous. It is called *salin*. This substance, calcined in a furnace, becomes white, and yields a good potash.

Ashes which have undergone no preparation are also made use of, and principally for leys. What has been said of potashes, may be applied to them.

The vegetables from which potash is extracted differ much from one another, both in the quantity of ashes which they yield on combustion, and in the proportion of potash found in their ashes. We shall give an outline of the observations which have been made on this subject, because they may guide us in the art of preparing potashes, and in their different applications to the arts.

It results, from the experiments of Pertuis in particular,\* that the herbaceous plants furnish in equal weight, after their drying, much more ashes than ligneous (woody) plants, and that the first contain a larger proportion of alkali; that the trunks of trees yield less than the branches, and the braches less than the leaves; but on this subject, as well as on several others relating to vegetation, much more extensive and exact researches than the above are to be found in a work just published by Theodore de Saussure.†

\* Ann. de chimie, tom. xix.

† Recherches chim. sur la vegetation. We find in this excellent work, observations which occasion some modifications in the explanations which we have given on the change produced by the air on the colouring particles, and the vegetable substances which suffer its action. The author has determined in a more positive manner the circumstances of this alteration.

Saussure, on exposing extracts and other vegetable substances to the action of the air in closed vessels, found that the volume of the air was not diminished, but that its oxygen

His experiments have placed beyond doubt, that potash, and the other salts which are found in the ashes of vegetables, are not a product of vegetation, but that they proceed from the soil from which they are absorbed, and even from the atmosphere. Consequently, the same vegetables which grow in different soils yield in their combustion a different proportion of ashes, which have different proportions of saline or earthy substances, either soluble or insoluble. The parts of vegetables leave more ashes, as they are subject to a greater transpiration; because these ashes proceed from the substances which were held in solution in the vegetable juice. Thence the leaves afford more than the bark; this more than the alburnum; and the alburnum more than the timber.

For the same reason herbaceous plants yield much more of it than the woody plants.

The proportions of the alkalies, or rather of the soluble part, vary in these ashes. The seeds contain most; the leaves come next; but when they are young they contain more. The bark has the smallest quantity of it. This quantity is seen to diminish, according as the rain water has dissolved and carried it away.

The phosphates, which the ashes of vegetables contain, form an important consideration. Saussure has found, that all vegetables contain the following phosphates: Phosphate of potash; phosphate of potash and lime, soluble like the preceding; and phosphate of lime, insoluble. As they usually contain carbonate of lime, changes of combination take place during incineration. The phosphate of potash is decomposed by the carbonate of lime; and there is found in the ashes only phosphate of lime or a smaller quantity of the first two combinations, than what existed in the vegetable. If different vegetable parts be inci-

was changed into carbonic acid, extracting its carbon, and combining with it. At the same time, a production of water takes place, by the more intimate combination of the hydrogen contained in this substance with the oxygen which was equally contained in it, and, of consequence, the substance contains a larger proportion of charcoal. The effect is therefore comparable, in this respect, to that of a slight combustion.

His observations, however, even prove that the fact is not general; the cils absorbed some oxygen. It would appear, that the action of oxygen does not produce uniform effects even on the substances which are not oily. But it will be necessary to distinguish, by new observations, the cases different in the mode, but uniform in the result, which is a predominance of carbon.

nerated, a result will be obtained, which is not the mean that would have been got by making the incineration separately. Thus the bean contains phosphate of potash, without carbonate of lime, and no phosphate of lime is found in its ashes. But if it be burned along with the stem, which contains carbonate of lime, there is obtained, instead of phosphate of potash, a much larger portion of phosphate of lime than the incineration of the stem alone would have given.

From these observations, some results may be drawn useful to our subject, which we abridge with regret.

1. For the fabrication of potash, it is more advantageous to collect herbaceous plants, leaves, and small sprigs of trees, than to burn the trunks themselves.

2. When the ashes are boiled into a condensed ley, in order to extract their potash, the alkali must convert a part of the insoluble phosphate of lime into phosphate of lime and potash; and the portion of the alkali which enters into this combination becomes inactive, by reason of the saturation which it experiences.

We shall not dwell on the other substances which enter into the composition of the ashes, and of ordinary potash; because the only matter which is useful and of importance to estimate is the alkaline. We have described, in treating of bleaching, the most exact means of arriving easily at this valuation. If there be an intention, however, of employing potash as an alternative or auxiliary, it may be proper to ascertain if it contains much carbonic acid, which its effervescence with acids points out. But a solution of it must be previously made to separate the effect of the potash from that of the carbonate of lime. The quantity of carbonic acid which escapes may be ascertained by verifying the loss of weight experienced by the mixture of potash and acid, whose separate weights had been determined beforehand.

## II.—Of Soda.

Chemists have given the name *mineral* to this alkali, because it is often found at the surface of the earth, or in subterraneous cavities. Thus a great quantity of it may be gathered in Egypt in the neighbourhood of lakes, called *natron*; a name also given



to the soda obtained from them. In several parts of Barbary, Syria, Persia, in the West Indies, China, and even in our climates, it is likewise found.

The conditions which determine this production, are, judging from the observations made near the natron lakes,\* a mixture of muriate of soda and carbonate of lime, in a moist ground, not too clayey, and a pretty hot temperature. In this case, a slight solution of carbonate of lime is effected, and the causes which favour the efflorescence peculiar to carbonate of soda, determine its separation, while a corresponding portion of muriate of lime infiltrates into the earth.

The soda thus collected in Egypt is not pure, but contains variable proportions of carbonate of soda, muriate of soda, sulphate of soda, and of earth, mingled, even when different specimens are taken on the same grounds.

The greatest part of the soda, however, which is made use of, is the product of the combustion of plants which grow on the sea-shores, and particularly of the *salsola soda*, Linn.

The most esteemed comes to us from Alicant. Some is also extracted from the same plant on our maritime coasts, as well as on others. To these sodas, according to the countries and plants from which they are got, different names are given; such as Rochette, Varech, Salicor. Julia has lately given an interesting description of the culture of the *salsola*, established in the environs of Narbonne, from which a soda comes, known under the name of Salicor.†

These sodas differ much from one another in the proportion of carbonate of soda. There are ashes of Varech which contain hardly any of it; but it is useless to dwell on these differences, because confidence can only be put in the chemical proof, which should be the same as for potash. A good soda, or a carbonate of soda, should be assumed for a term of comparison; because a larger proportion of acid is required to saturate a quantity of soda, than an equal weight of potash.

Soda is in the state of a carbonate, or most part of it at least is in that state, when plants are incinerated. It crystallizes, retaining much water of crystallization; but it parts with this

\* Mémoire sur l'Egypte.

† Ann. de chimie, tom. xlix.

easily to the air, and falls thereby into efflorescence, with the loss of nearly one-half its weight.

This difference distinguishes it from potash, which naturally retains, after incineration, only a part of the carbonic acid necessary to its crystallization; and which, till it be saturated with it to this point, attracts, on the contrary, the humidity of the air; a difference apparently depending on the stronger affinity which soda exercises on the acids, and on the greater condensation which it produces, particularly on those that are naturally elastic.

Although the native carbonate of soda crystallizes and dries in the air, it retains, however, weak alkaline properties, and greens the colours that characterize them. But it may take a larger proportion of carbonic acid. The celebrated Klaproth has observed in a species of carbonate of soda, or natron, a proportion of carbonic acid, nearly double that obtained from the ordinary carbonate. Hence its alkali is in a different state of saturation. Probably it would not afford marks of alkalinity. It might be found perhaps acidulous. It does not effloresce.

As soda contains not only a good deal of foreign salts, but a greater or less proportion of sulphuret, it is right to employ it for certain operations of dyeing in the state of a pure carbonate. It is then called *salt of soda* (crystals of soda).

In order to free soda from the foreign substances, it is to be dissolved in water, and the different salts are to be separated as they precipitate or crystallize. The crystals of carbonate of soda form last of all.

When this salt is used, it is essential to pay attention to the state in which it exists; for when it is in crystals it contains one-half (fully 3-5ths) its weight of water of crystallization. Hence, when it has effloresced, one part produces as much effect as two parts of crystals.

Lime acts on this salt in the same manner as on carbonate of potash; that is to say, it robs it of the greater portion of its carbonic acid, rendering it caustic. In this state it is pure soda, (for the small quantity of carbonic acid which it retains may be neglected), the soda of chemists, the ley of the soap-boiler.

Sometimes the name of strong water, or strong liquor of the soap-boilers, is given to a solution of caustic soda. Such a

denomination may easily lead to mistakes, making this alkaline solution be confounded with nitric acid, called also *eau forte*, (strong water, or aquafortis). Hellot tells us that he was deceived in this way, in the preparation of a vat of indigo, which had been suggested to him.

Since soda exerts on acids a stronger action than potash, it may probably produce also a greater effect on colouring substances when it is pure; but its alkaline action is much more moderate when it is in the state of carbonate, for it is then in a high degree of saturation, and possesses uniform properties. From this circumstance it should therefore be preferred to potash, which has less carbonic acid, containing variable quantities of it in the state in which it is extracted.

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## CHAPTER VIII.

### *Of Soap.*

SOAP is the combination of an alkali with an oil. Alkali deprived of carbonic acid must be employed for its formation; for this acid may eliminate its oil in combining with the alkali. We must begin, therefore, with stripping it of its combined carbonic acid. In the work-shops the name *soap-ley* is then given to it.

To make this ley, the soda which is used for hard soap is treated with a suitable proportion of lime, usually two of lime for one of soda. A succession of waters is passed through the same mixture. The last, which are least charged, are employed the first in the boiling with oil; because the coagulation which would be formed at first with too strong a ley, would obstruct the uniformity of the combination.

We have remarked, that the caustic alkali, prepared with quicklime, retained a portion of its carbonic acid; which, on treating the caustic ley with oil, converts a part of the alkali into a carbonate that cannot enter into the compound. Whenever the formation of the soap is advanced, the portion of ley converted into carbonate, which may serve anew to make a caustic ley with quicklime, is run off by a stopcock placed in the lower part of the boiler. Strong ley is then added. When

it is ascertained from samples that the consistence of the soap is sufficient, it is drawn out and run into a species of wooden moulds, where it cools, and takes the form adapted to commerce. But before this last operation, a certain quantity of muriate of soda is added, which facilitates the separation of the soap from the aqueous liquid (spent ley).

This preparation may be made in the cold, but it is longer and less easily finished.

Recent soap contains a great deal of water, which it loses by desiccation. Fraudulent dealers endeavour to sell it with all this weight; and to preserve it in this state, they keep it in a moist place, even in water saturated with sea-salt. This brine does not dissolve it, but merely confines in it the whole water that it can hold. For separating, by this property, the soap from its solution in the boiler, the muriate of soda was added towards the end, as we have stated. The redundancy of water is discovered by keeping the soap in a dry and warm place, where it soon loses what is superfluous. Starch, or other foreign substances, are sometimes mixed with soap, in order to augment its weight.

Marbled veins are given to soap by adding, before it has assumed consistency, a little sulphate or red oxyde of iron, which probably forms some metallic soap, that is unequally mixed with the paste. Soap becomes harder by this means, and retains less water.

The general properties of compounds are recognized in soap. Thus soda, which produces, as we have seen, a greater effect with the acids, comports itself in the same way with the oils, thereby forming soaps, harder and less soluble than those which have potash for their base. In consequence of this greater insolubility, if muriate of soda be added to a solution of soap made with potash, the soda takes the place of the potash, and it is a soap with base of soda which coagulates and separates, as Darcet, Pelletier, and Lelievre observed, to whom we owe a very good description of the preparation of soap.\*

The oils contribute, on the other hand, to the qualities of the combination which they form with the alkalis: thus the fatty substances naturally solid, such as tallow, lard, and butter,

\* *Mémoires de chimie*, tom. xix. (*Annales*?)

form solid and firm compounds ; olive oil, which has a tendency to become solid whenever its temperature is lowered, affords a hard soap, which makes it be preferred, for this species of soap, (to which, in other respects, it communicates no disagreeable smell or colour), to the other oils, which being less consistent, yield softer soaps, commonly coloured.

If oils be combined with bases naturally disposed to take the solid state, such as lime, magnesia, barytes, metallic oxydes, insoluble soaps are formed ; but this insolubility is an obstacle that prevents the combination from being directly formed with accuracy. The solution of an alkaline soap must be taken, and lime, barytes, or strontian water poured into it. These alkaline earths take a portion of the oil from the soluble alkalies to form an insoluble soap, which separates. Instead of the aqueous solution of these bases, their solution in an acid may be taken. In this case an exchange of base occurs, and the earthy combination is more completely formed. The latter method must be employed for the bases insoluble in water, such as magnesia, and the metallic oxydes.

The uses for which soap is employed lead sometimes to the preference of a hard, and sometimes of a soft soap. The first is prepared with soda and olive oil. It ought to be white. This soap is used in the ungumming (scouring) of silk.

To make soft soap, oil of colza, turnip seed, or fish oil, is employed. The cheapest at the place of the manufacture is generally chosen. But as softness is the quality now desired, potash is used instead of soda. Whiteness is of no consequence to this soap ; and the oils made use of commonly impart a greenish or even blackish colour, whence the article is called green or black soap.

This soap is chiefly used in the bleaching of cloths and raw yarns ; and in the operation of fulling woollens.

For the latter purpose, a less costly combination may be employed, possessing the deterative properties of soap ; this is the solution of an animal substance in potash. Chaptal observed,\* that potash which has been saturated with fragments of wool formed this species of soap, which might be advantageously substituted for ordinary soap. The odour which it communicates to cloth is dissipated by washing and exposure to the air.

\* Mémoires de l'institut. tom. i.

## CHAPTER IX.

*Of Sulphur.*

SULPHUR exposed to a certain heat volatilizes, and then resumes the solid state by the contact of cold bodies. Thus it is reduced to subtile molecules, called flowers of sulphur. This preparation is made in the small apparatus of the laboratory ; or on the great scale, in a kind of chimneys or chambers, where it attaches itself to the cool walls.

When sulphur is exposed to a more elevated temperature, it combines with oxygen, passing thereby to the state of an acid ; but this acid differs according to the elevation of the temperature, or the vivacity of the combustion. When the temperature is not sufficiently high, sulphurous acid is obtained.

Sulphurous acid differs from sulphuric, 1. From the oxygen in it being less condensed, so that the combination retains a pretty great elasticity, and dissolves in only a small quantity in water : 2. From the proportion of its oxygen being smaller than in sulphuric acid, but, at the same time, this element experiences a much weaker action on the part of the sulphur ; a circumstance which has great influence on its characteristic properties.

The oxygen is retained, therefore, much more feebly in sulphurous than in sulphuric acid. Hence several substances, which do not take oxygen from sulphuric acid, decompose the sulphurous. It inclines, in this respect, to the properties of chlorine, although it does not give up its oxygen so easily, but, on the contrary, carries off that of the chlorine, in order to pass to the state of sulphuric acid. In like manner, it inclines to the properties of nitric acid.

Sulphurous acid, or the combination of the sulphurous gas with water, is not employed in the processes of dyeing ; but the vapour formed directly by the combustion of sulphur is used. In this state of gas, it exercises a more lively action, for it whitens the flowers, which, in its liquid state, it reddens like the other acids. It would be wrong, therefore, to substitute liquid sulphurous acid for the fumes of burning sulphur, as has been proposed. There are circumstances, however, where a different or more moderate effect might be wished for, in which

it would be advantageous to employ it in the liquid state. We have seen one example of this in the process of Giobert for bleaching raw silk.

For obtaining it in this state there is a more convenient and easier means than by the combustion of sulphur; that is, merely to mix with sulphuric acid a vegetable substance containing hydrogen, as sugar, and to distil, receiving the vapour that is disengaged into the bottom of a receiver, by means of a tube. Heat, which tends to produce elastic combinations, determines a formation of water, at the expense of the hydrogen of the sugar, and a production of sulphurous acid, which issues to combine with the cold water. But there is formed at the same time a little carbonic acid; of no importance to the operations for which the liquid acid is intended. Besides, when the sulphurous acid acquires a certain condensation, it expels the carbonic acid from the water.

Sulphuring, or exposure to the fumes of burning sulphur, is employed to give the utmost whiteness to silks and woollens intended for white stuffs.

For the sulphuring process an insulated chamber, having no chimney, is made choice of, through which, on occasion, a current of air may be sent.

For 110 pounds of silks stretched on perches, placed at a height of rather more than two yards, nearly two pounds of sulphur, reduced to a coarse powder, are put into an earthen or iron pot, at whose bottom there is a little ashes. This powder is set fire to in several places. The chamber is well closed, to prevent the dissipation of the sulphurous fumes. Next day, the windows are thrown open to let them escape, and to dry the silk. But in winter, after the smell of the sulphur has gone away, the windows are re-shut, and burning charcoal is introduced, in chafing-dishes, to make the silk dry.

This operation gives the silk not merely a great whiteness, but at the same time creakiness or rustling in handling, (*du cri ou du maniemment*,) that is to say, a species of tremulous elasticity, which is perceived on pressing it between the fingers.

As the *maniemment* gives a certain stiffness to silks, those must not be sulphured which are to be *watered*, because they would give too much resistance to the impressions of the calendar, under which the silks are passed to give them the undulations.

In like manner, sulphuring cannot be applied to silks intended for the hat manufactory, because they would corrode the iron and steel of the tools with which they are to be worked, and occasion rust.

Sulphured silk takes on most colours badly; and, therefore, previously to dyeing, it must be freed from sulphur, by repeated soaking and shaking over in hot water.

When silk is sulphured, if it be thought not to have sufficient azure for the wished for shade, it must be azured a second time in clear water, without addition of soap, and then again sulphured.

These properties of the sulphured silk are owing to the sulphurous acid which has combined with it, whose presence may be made perceptible by means of sulphuric acid, which immediately disengages sulphurous vapours from it. The sulphuring of woollen cloth is executed in nearly the same manner as that of silk; but it is to be remarked, that if this operation be not performed with precaution, and that if the combustion of the sulphur takes place with too much rapidity, sulphuric acid is formed, which falling down in drops, corrodes the cloth,—an inconvenience not easily avoided.

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## CHAPTER X.

### *Of Waters.*

THE quality of the waters is an essential object in dyeing; but it is perhaps less important to make known the injurious effects which they may produce, than to destroy the prejudices to which they have often given rise. Thus peculiar properties have been ascribed to the water of the Bievre, which supplies the manufactory of the Gobelins; but Guillaumot remarks, that when this little river is too low, the water is drawn from the Seine, without seeming to render the dyes less beautiful.

It is superfluous to say, that the waters used in dyeing must not be muddy, or contain putrid substances; that waters so much charged with foreign matters, as to be ranked among mineral waters, easily distinguishable by the taste, must not be



employed. With these exceptions, waters act on the colouring particles principally by the earthy salts they contain, which render the colours in general deeper and more dull.

The carbonates of lime and magnesia have, moreover, the inconvenience of being thrown down during the ebullition, which expels the excess of carbonic acid that held them in solution. Thus these earths applied to the stuffs darken them, and prevent the colouring particles from penetrating.

It is of importance therefore, to ascertain these species of waters, called hard or crude, in order to avoid them in most dyes. Chemists possess methods, not only of determining the different principles contained in waters, but even of assigning with precision the quantity of each; but the precautions requisite for this analysis, in general demand a profound knowledge and experimental dexterity, which persons engaged in dyeing cannot be presumed to possess. Happily a trivial and easy test is sufficient to show whether a water contains an injurious quantity of these salts. This is, the solution of soap.

All the salts having an earthy base decompose soap by an exchange of bases. Their earth unites to the oil, while their acid combines with the alkali of the soap; and from the combination of the oil and the earth, a soap with earthy base results, which being insoluble in water, forms the clots, (or mottling,) which are in that case observable.

Whenever, therefore, a water is limpid, when its flow is constant, when it has no sensible taste, and dissolves soap well, it may be regarded as very proper for dyeing; and all such as possess these qualities are equally suitable.

But since a choice of waters is not always equally at command, methods have been sought for correcting such as were bad, at least to a certain degree, particularly for the purpose of dyeing delicate colours. With this view, water in which bran has been fermented, called sour water, is principally used.

It appears that sour water acts by decomposing the carbonates of lime and magnesia, its acid expelling the carbonic acid. The earthy sediment which forms during ebullition is thus obviated.

Mucilaginous plants are also boiled along with the water to be corrected, when a froth forms, that is skimmed off. The mucilage coagulates, carrying with it the earths which separate on the volatilization of the carbonic acid, as well as such as are merely mixed with the water, and which render it turbid.

The salts with an earthy base, which are in general injurious to dyeing, may in certain cases be useful, serving to modify the colours when our object is to obtain deep shades.

As the water of a river may contain more or fewer salts with an earthy base, according as its bed is higher or lower, it happens sometimes that on following exactly the same process the same shade is obtained only at certain periods ; or some modifications are required to be made in the process to obtain the same result, according to the state of the river.

The waters which decompose soap, and form a soap of lime, are disadvantageous to bleaching, not merely by the waste of the soap uselessly decomposed, but principally because the calcareous soap, which is insoluble in water, fixes on the stuff, gives it a greasy feel, renders it at the same time yellow, and shakes off in small scales. This inconvenience is obviated by decomposing the earthy salts with a little carbonate of soda or potash.

## PART II.

### OF THE PROCESSES OF ART.

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#### SECTION I.

##### OF BLACK.

#### CHAPTER I.

##### *Of the Processes for Dyeing Black.*

VERY few substances are known which can afford of themselves a solid black; and they have been tried only on linen and cotton. The juice of the cashew nut, or *anacardium* of India, communicates a black colour, which resists, not only washing, but even boiling with soap and alkaline leys: It is used for marking linen. The *anacardium occidentale* affords also a durable dye, but it is merely brownish.

The *toxicodendron* yields a juice which produces nearly the same effect. The juice of the stems of hop affords a very durable brownish-red colour. Sloe juice gives a pale tint bordering on brown, which, washed several times with soap, and then moistened with solution of alkali, becomes of a deeper brown. On boiling sloes, their juice becomes red; and the red dye which it imparts to linen, changes, when washed with soap, into a bluish colour, which is permanent.\*

According to Linnæus,† the juice of the berries of the *æctea spicata*, or *cristophoriana*, makes a black ink with alum; and the berries of the *impetrum procumbens*, or *erica baccifera nigra*, produce with alum a black colour bordering on purple.

A tree grows in the Brazils, which the botanists call *pomi-*

\* Lewis' Exper. Phys. et chym. tom. ii.

† Amœnit. Academ.

*fera indica tinctoria*, or *genipa Americana*, whose berries and leaves dye a black-blue, which resists the action of soap.

The methods just mentioned of obtaining a black colour cannot be employed in dyeing, because the substances from which it is derived cannot be collected in sufficient quantities for the necessities of the art, and because the black which they afford is not comparable to that formed in the dyehouse. All black dyes are the result, therefore, of an artificial combination. The black molecules which are produced by the union of the astringent principle, or of another colouring substance, and the oxyde of iron, combine with the stuffs. We shall proceed to detail the principal processes by which this operation is performed on different kinds of goods.

According to the process which Hellot describes,\* for dyeing woollen cloth black, it must receive the deepest blue, or mazarine blue, be washed in the river on coming out of the vat, and then cleansed at the fulling-mill.

For 110 pounds of cloth there are put into a boiler, of middle size,  $17\frac{1}{2}$  pounds of logwood, with as much Aleppo galls in powder, and the whole being enclosed in a bag, is boiled in a sufficient quantity of water for twelve hours. One-third of this bath is transferred into another boiler with 2 pounds 3 ounces of verdigris; and the stuff is passed through this solution, stirring it continually during two hours, taking care to keep the bath very hot without boiling. The stuff is then lifted out, another third of the bath is added to the boiler, along with 9 pounds of sulphate of iron or green vitriol. The fire is to be lowered while the sulphate dissolves, and the bath is allowed to cool for half an hour, after which the stuff is introduced, and well moved about for an hour, after which it is taken out to air. Lastly, the remaining third of the bath is added to the other two, taking care to squeeze the bag well: 17 to 22 pounds of sumach are thrown in; the whole is just brought to a boil, and then refreshed with a little cold water; 2 pounds 3 oz. more of sulphate of iron is added, after which the stuff is turned through for an hour. It is thereafter washed, aired, and put again into the bath, stirring it continually for an hour. After this, it is carried to the river, washed well, and then fulled. Whenever

the water runs off clear, a bath is prepared with weld, which is made to boil for an instant; and after refreshing the bath, the stuff is turned in to soften it, and to render the black more fast. In this manner, a very beautiful black is obtained, without rendering the cloth too harsh.

Commonly more simple processes are employed. Thus the blue cloth is simply turned through a bath of gall-nuts, where it is boiled for two hours. It is next passed through a bath of logwood and sulphate of iron for two hours, without boiling, after which it is washed and fullled.

Hellot has found that the dyeing might be performed in the following manner:—For 18 metres (yards nearly) of dark blue cloth, a bath is made of  $1\frac{1}{2}$  pounds of fustic (*morua tinctoria*),  $4\frac{1}{2}$  pounds of logwood, and 11 pounds of sumach. After boiling the cloth in it for three hours, it is lifted out, 11 pounds of sulphate of iron are thrown into the boiler, and the cloth is then passed through it during two hours. It is now aired, and put again into the bath for an hour. It is lastly washed and scoured. The black is less velvety than that of the preceding process. Experience convinced him, that the maddering prescribed in the ancient regulations only gives a reddish cast to the black, which is obtained finer and more velvety without madder.

A black may be dyed likewise without having given a blue ground. This method is employed for cloths of little value. In this case they are *rooted*, that is to say, they receive a dun ground with walnut husks, or the root of the walnut tree, and are afterwards made black in the manner above described, or in some other way; for it is obvious, that a black may be obtained by several processes. (NOTE FF.)

According to Lewis, the proportions which the English dyers most generally adopt are, for 110 pounds of woollen cloth previously dyed of a dark blue, about  $5\frac{1}{2}$  pounds of sulphate of iron, as much gall-nuts, and 33 pounds of logwood. They begin by galling the cloth, they then pass it through the decoction of logwood, to which the sulphate of iron has been added.

When the cloth is completely dyed, it is washed in the river, and passed through the fulling-mill till the water runs off clear and colourless. Some persons recommend, for fine cloths, to full them with soap water. This operation requires an expert workman, who can free the cloth thoroughly from the soap.

Several recommend at its coming from the fulling to pass the cloth through a bath of weld, with the view of giving softness and solidity to the black. Lewis says, that passing the cloth through weld, after it has been treated with soap, is absolutely useless, although it may be beneficial when this operation has been neglected.

We read in the Memoirs of Stockholm for the year 1753, that for nutgalls may be substituted the *uva ursi*, gathered in autumn, and dried with care so as to keep its leaves green. 110 pounds of wool are to be boiled for two hours with 17 pounds of sulphate of iron, and as much tartar; the cloth is rinsed on the following day, as after alluming. 165 pounds of *uva ursi* are then boiled in water for two hours. After removing it, a little madder is introduced, and the cloth is at the same time immersed in the decoction, in which it is left for an hour and a half, or an hour and three quarters, and thereafter rinsed in water. Lewis remarks, that this manner of dyeing gives a good enough black on blue cloth, but merely a dark brown on white cloth; and that the madder and tartar are of no use. The *uva ursi* throws down the iron in coarse black particles, which float through the water.

Different operations may be distinguished in dyeing silk black; the boiling of the silk, its galling, the preparation of the bath, the operation of dyeing, the softening of the black.

Silk, as we have seen, PART I. p. 101, naturally contains a substance called *gum*, which gives it the stiffness and elasticity peculiar to it in its native state; but this adds nothing to the strength of the silk, which is then styled *raw*; it rather renders it, indeed, more apt to wear out by the stiffness which it communicates; and although raw silk more readily takes a black colour, yet the black is not so perfect in intensity, nor does it so well resist the reagents capable of dissolving the colouring particles, as silk which has been (*decreussée*) scoured or deprived of its gum.

To cleanse silk intended for black, it is usually boiled four or five hours with one-fifth of its weight of white soap, after which it is carefully beetled and washed.

For the galling, nut-galls equal to nearly three-fourths of the weight of the silk are boiled during three or four hours; but on account of the price of Aleppo galls, more or less of the white

gall-nuts, or of even an inferior kind called *galon*, berry or apple-galls are used. The proportion commonly employed at Paris is, two parts of Aleppo galls to from eight to ten parts of *galon*. After the boiling, the galls are allowed to settle for about two hours. The silk is then plunged into the bath, and left in it from twelve to thirty-six hours, after which it is taken out and washed in the river.

Silk is capable of combining with quantities, more or less considerable, of the astringent principle; whence results a considerable increase of weight, not only from the weight of the astringent principle, but also from that of the colouring particles, which subsequently fix themselves in proportion to the quantity of the astringent principle which had entered into combination. Consequently, the processes are varied according to the degree of weight which it is wished to communicate to the silk; a circumstance requiring some illustration.

The commerce of silk goods is carried on in two ways: they are sold either by the weight or by the surface, that is, by measure. Thus the trade of Tours was formerly distinguished from that of Lyons; the silks of the former being sold by weight, the latter by measure. It was therefore their interest to surcharge the weight at Tours, and, on the contrary, to be sparing of the dyeing ingredients at Lyons; whence came the distinction of light black and heavy black. At present, both methods of dyeing are practised at Lyons, the two modes of sale having been adopted there.

Silk loses nearly a fourth of its weight by a thorough boiling, and it resumes, in the light black dye, one-half of this loss; but in the heavy black dye, it takes sometimes upwards of a fifth more than its primitive weight; a surcharge injurious to the beauty of the black, and the durability of the stuff. The surcharged kind is denominated English black, because it is pretended that it came to us from England. Since silk dyed with a great surcharge has not a beautiful black, it is usually destined for weft, and is covered (blended) with a warp dyed of a fine black.

The peculiarity of the process for obtaining the heavy black, consists in leaving the silk longer in the gall-liquor, in repeating the galling, in passing the silk a greater number of times through the dye, and even letting it lie in it for some time. The first galling is usually made with galls which have served for a pre-

ceding operation, and fresh gall-nuts are employed for the second. But these methods would not be sufficient for giving a great surcharge, such as is found in what is called the *English black*. To give it this weight, the silk is galled without being ungummed; and on coming out of the galls, it is rendered supple by being worked on the jack and pin, (*chevillages*.)

The silk-dyers keep a black vat, and its very complex composition varies in different dye-houses. These vats are commonly established for many years; and when their black dye is exhausted it is renovated by what is called a *brevet*. When the deposite which has accumulated in it is too great it is taken out, so that at the end of a certain time nothing remains of the several ingredients which composed the primitive bath, but which are not employed in the *brevet*. The description of a bath and *brevet* of this description may be seen in the work of Macquer.\* There entered into it seeds of fœnugreek, of psyllium, (fleawort,) cummin, colocynth, the berries of buckthorn, agaric, nitre, muriate of ammonia, sal gem, litharge, lead ore, orpiment, corrosive muriate of mercury, &c. Macquer acknowledges that there are many useless ingredients in this process; and in fact several of them are no longer admitted. But the compositions not only of every country, but of every dyehouse differ.

Iron filings are usually added to the dyeing bath; but some dyers, particularly at Tours, substitute for them the *moulée*, or the abraded dust of grindstones; this *moulée* probably acts merely by the particles of iron which it contains in a very comminuted state.

While the silks are getting the preparatory treatment for dyeing, the bath is heated, taking care to stir it from time to time, in order that the *marc* (sludge or sediment) at the bottom may not become too hot. This bath should never be raised to ebullition. More or less gum and solution of iron are added, according to the different processes; and when it is judged that the gum is dissolved, and that the bath has arrived at a degree approaching to ebullition, it is allowed to settle for about an hour; the silks are then plunged into it, usually divided into three portions, that they may be immersed successively in the bath. Each portion is slightly wrung three times, and each

\* Art de la teinture en soie.



time hung up to air. The object of this operation is to squeeze out the liquor with which the silk is impregnated, and which is exhausted, and to make fresh liquor penetrate it; but above all to expose the silk to the atmosphere, which deepens the black.

After each portion of the silk has experienced three wringings, the bath must be heated anew, putting into it again gum and sulphate of iron, as at first. The operation performed in the interval from one heating to another, is called *a fire*, (*un feu*.) Only two fires are given for a light black, but three for a heavy black; and the dyers let the silk remain in the bath, even after the last fire, for about twelve hours. Sixty-six pounds are usually dyed in one operation, which is called *a heat*, (*chaudée*.) If only the half of this quantity be dyed, there is occasion for no more than one fire for the light black.

The dyeing operation being finished, a little cold water is put into a tub, in which the silk is washed by turning or shaking it over the rods, (*on disbrode la soie en la lisant*.)

The silk, on coming out of the bath, has a great deal of harshness. The operation by which it is freed from this, is termed the *softening*. Into a large vessel, nearly full of water, a solution of soap is poured, in the proportion of from 4 to 5 pounds of soap for every 110 pounds of silk. The solution of soap is strained through a cloth into the water, and is well mixed with it. The silk is then introduced, and left for about a quarter of an hour, after which it is wrung out and dried.

For the dyeing of raw silk black, it is galled in the cold with the bath of galls which have already served for the black of boiled silk. For this purpose, silk in its native yellow colour is made choice of. It should be remarked, that when it is desired to preserve a portion of the gum of the silk, which is afterwards made flexible, the galling is given with the hot bath of gall-nuts in the ordinary manner. But here, where the whole gum of the silk, and its concomitant elasticity are to be preserved, the galling is made in the cold. If the infusion of galls be weak, the silk is left in it for several days.

Silk thus prepared and washed takes very easily the black dye, and the *disbrodure*, (rinsing in a little water,) to which sulphate of iron may be added, is sufficient to give it. This dye is made in the cold; but according to the greater or less strength of the rinsings, (*disbrodure*,) it requires more or less time. Occasion-

ally three or four days are necessary; after which it is washed, beetling it once or twice, and it is then dried without wringing, to avoid softening it.

Raw silk may be more quickly dyed, by shaking it round the rods in the cold bath after the galling, airing it, and repeating these manipulations several times; after which it is washed and dried as above.

Macquer describes a more simple process for the black, with which velvet is dyed at Genoa, and he says that this process, rendered still simpler, has had complete success at Tours. The following is his description.

For 110 pounds of silk, 22 pounds of Aleppo galls, in powder, are boiled for an hour in a sufficient quantity of water. The bath is allowed to settle till the galls have fallen to the bottom of the boiler, from which they are withdrawn; after which 33 pounds of English vitriol (copperas) are introduced, with 13 pounds of iron filings, and 22 of country gum, put into a kind of two-handled colander pierced every where with holes. This kettle is suspended by two rods in the boiler, so as not to reach the bottom. The gum is left to dissolve for about an hour, stirring it from time to time. If after this time some gum remains in the kettle, it is a proof that the bath, which contains two hogshheads, has taken as much of it as is necessary. If, on the contrary, the whole gum is dissolved, from 2 to 4½ pounds more may be added. The colander is left constantly suspended in the boiler, from which it is removed only when the dyeing is going on; and thereafter it is replaced. During all these operations the boiler must be kept hot, but without boiling. The galling of the silk is performed with one-third of Aleppo galls. The silk is left in it for six hours the first time; then for twelve hours. The rest, *secundum artem*.

Lewis states, that he has repeated this process in the small way; and that by adding sulphate of iron progressively, and repeating the immersions of the silk a great number of times, he eventually obtained a fine black.

The sulphate of iron, indeed, seems to be in too small proportion, in the process described by Macquer; and some inconveniences must undoubtedly have been found in it, since its practice has not been retained at Tours. Lewis thinks that the gum is of no use, and that it is all carried away in the washing

of the silk ; but if he had continued to dye in the same bath, he would probably have perceived that it served to maintain it. It appears, however, that an excess of it had been used in that process. It must assuredly be advantageous, when the quantity of gum is diminished, to add the sulphate of iron in portions, after each *fire* (*chaque feu.*) Lewis remarks, moreover, that although a good black may be dyed on white silk, without making use of logwood or verdigris, the addition of these two ingredients contributes greatly to improve the colour on silk as well as on wool.

The process of dyeing black on silk is very expensive, from the quantity of galls, as their price is much raised. It is of consequence, therefore, to try to lessen its quantity. We shall advert to a process extracted from the memoir of Anglès, which competed for a prize proposed by the Academy of Lyons in 1776, in which this object was attempted.

The silk, boiled with care and washed in the river, is plunged into a strong decoction of green walnut peels, in which it is left till the colour of the bath be exhausted. It is then withdrawn to be slightly wrung on the pins, dried, and washed in the river. The decoction of the walnut husks is made by boiling for a full quarter of an hour; after which it is taken from the fire, and the froth is allowed to fall before plunging in the silk, which should have been previously soaked in tepid water. The blue ground is given by means of logwood and verdigris, dissolving in cold water one part of verdigris for sixteen of silk. This is allowed to steep in it for two hours, and it is then passed into a strong decoction of logwood. It is gently wrung out and dried, previous to its being washed in the river. For a light black, the galling may be dispensed with; but for obtaining a heavy black, the silk must be galled with half its weight of gall-nuts.

To prepare the bath, 2 pounds of nut-galls, and 3 pounds of sumach, are macerated in 22 gallons of water, over a slow fire, for twelve hours. Whenever the bath has become clear, 3 pounds of sulphate of iron, and as much gum arabic, are dissolved in it. The solution being made, the silk is plunged in at two successive times; and is allowed to remain each time for two hours, taking care after the first immersion to air and dry it before giving it the second fire; after which it is aired and dried equably. Two

beetlings in the river are now given ; after this it receives the third fire, in the same manner as the two preceding, except that it is left four or even five hours in the bath. When it is drained and dried, two other beetlings are given in the river. Care must be had that during the operation the degree of heat do not exceed the middle term between freezing and boiling water, which corresponds to 40° R. (122° F.) ; and before giving the last two fires, half-a-pound of sulphate of iron, and as much gum arabic, must be added.

To remove the harshness that the black dye imparts to silk, Anglès prefers the decoction of weld to the solution of soap.

He says, that the blue of indigo given to silk before the black dye, allows it to take only a mealy black, but that with logwood and verdigris a velvety black is obtained. He also says, that green walnut peels soften silk. Although a fine black may be formed with walnut peels, and the bath which has been described, he adds to it, however, the logwood and verdigris, in order to save the necessity of employing much sulphate of iron, which weakens the silk too much. Lastly, he thinks that nut-galls serve merely to give weight to the silk, and that sumach is sufficient for this dye.

Linen and cotton take with difficulty a sufficiently deep black, that will resist soap. Hence we are obliged to employ peculiar processes for dyeing them black ; and hitherto few such dyes have been found to give satisfaction.

For dyeing cotton and linen black, a solution of iron is made use of, which is kept in a cask called the black cask.\* This solution is prepared either with vinegar or small beer, or with the washings of pressed grapes, which is soured with rye-meal or other ingredients, with the view of getting an acid liquor at the lowest price. Old iron is thrown into this liquor, and the solution is set aside, to be used on occasion, taking care not to employ it till six weeks or two months from its preparation. Astringents are often added to this bath, and particularly the decoction of alder bark, which, even alone, has the property of dissolving a considerable quantity of oxyde of iron.

We remarked, in speaking of the acetate of iron, that this metal should be highly oxydized. It is consequently proper to

\* See Part I. p. 227.

separate the solution after it is made, from the metal below, which opposes its oxygenation.

Le Pileur d'Apligny describes the process\* followed at Rouen, for linen and cotton yarns. They are first dyed sky-blue in the vat, then wrung out, and set to dry. They are galled in the proportion of one part of gall-nuts for four of yarn. They are left twenty-four hours in the gall liquor, then wrung out anew, and set to dry.

About  $2\frac{1}{2}$  gallons of the black cask for every 2 pounds of yarn, are then poured into a tub. In this, the yarn is turned on the sticks, and worked with the hand in portions for about a quarter of an hour; it is then wrung out and aired. This operation is twice repeated, adding each time a new dose of the black cask, which should be skimmed with care. The yarn is aired once more; it is then wrung out, and washed in the river to cleanse it well, and dried.

To complete the dyeing of the yarn, a weight of alder bark, equal to that of the yarn, is boiled for an hour in a copper, along with a sufficient quantity of water. To this are added about one-half of the bath which has served for the galling, and sumach equal to one-half the weight of the alder bark. The whole is made to boil anew for the space of two hours, after which this bath is passed through a searce. When it is cold, the yarn is turned through it on the sticks, and it is worked in it by portions at a time. It is aired occasionally, then it is let down into the bath, where it is left for twenty-four hours. It is now wrung out and dried.

In order to soften this yarn after it is dry, it is the practice to steep it, and work it in the residuum of a bath of weld, which has served for other colours, to which a little logwood is added. It is taken out and wrung, and immediately turned through a tub of warm water, into which one part of olive oil for sixteen of yarn has been poured. It is finally wrung out and dried.

Le Pileur d'Apligny describes a process in which he makes use also of madder, to give linen and cotton yarn a black colour, which he speaks of as very beautiful, and very durable.

The yarn is first of all scoured in the ordinary way, galled, alumed, then turned through a bath of weld. On coming out

\* L'Art de la teinture des fils et étoffes de coton.

of this bath, it is dyed in a decoction of logwood, to which one-fourth part of sulphate of copper must be added for one part of yarn. On quitting this bath, it is washed in the river, and wrung repeatedly, without twisting it too strongly. Lastly, it is dyed in a bath made with one part of madder for two of yarn. To render the black not liable to change, the yarn must be turned through a bath of boiling soap water.

Wilson describes the manner pursued at Manchester, as follows:\* a galling is given with nut-galls or sumach, after which the dyeing is performed with the liquor of a bath composed of a solution of iron in a vegetable acid, formed not unusually with alder bark and iron; and then the goods are turned through the decoction of logwood with a little verdigris. The process is repeated till a deep black be obtained. It is necessary to wash and dry between each operation.

Mr. Bancroft had announced, that the acid of tar was employed at Manchester for black dyes on cotton. Chaptal, in his dyes, used pyrolignous acid; but to Bosc we owe the details of the operation by which he himself obtained a fine black by means of that acid.†

“Fill a cast iron boiler with pyrolignous acid; add to it old iron, well oxydized, and boil. The solution of the oxyde will take place rapidly. When the iron grows clean, and the solution black as ink, throw the whole into a cask, to be employed at need. Prepare your cotton as usual, by giving it a blue ground. Gall; turn the hanks of cotton through a bath of solution of pyrolignite of iron diluted with tepid water. Renew the gallings, and the turnings through the bath of pyrolignite of iron, till you have obtained a deep and brilliant black. Finish by passing your cotton through olive oil. This operation is simple. Throw on some tepid water a little olive oil; pass the cotton through this bath; it absorbs the oil; but it must be worked for a long time in the bath to diffuse the oil equally. This process softens, and gives suppleness to the cotton, as well as a great deal of brilliancy. Dry in the shade. The cottons are now of a perfect and very durable black. Every time that the bath of pyrolig-

\* An Essay on Light and Colours, and on what the colouring matters are that dye cotton and linen.

† Annales des arts et manufactures, tom. v.

nite of iron has been employed, it must be thrown away as useless, and the old baths are never to be added to the cask."

Bosc intimates, that the stuffs dyed by means of pyrolignous acid, retain, with much tenacity, the odour of this acid, and that they must be exposed for some time to the air to rid them of it, before folding them up for packing.

The application of oil, which heightens the black, and imparts softness to the stuffs, is given to those which are woven, for example, to cotton velvet, by means of brushes, which are slightly imbued with it at their surface.

Hermstadt\* recommends a process of Vogler, which consists in making use for a mordant of a solution of nitrate of lead, in turning the stuff through a solution of glue, and in dyeing it in a bath composed of gall-nuts, logwood, and sulphate of iron, for which last the acetate may be substituted.

## CHAPTER II.

### *Observations on the Processes for Dyeing Black.*

WE have dwelt at sufficient length on the reciprocal action of astringents and the oxyde of iron, and on the production of the molecules, which, attaching to stuffs, dye them black. But though the theory can lead to satisfactory explanations on this subject in general, it should be advanced with diffidence when it is to be applied to the processes of art. Circumstances unperceived, properties apparently slight, may influence the results sufficiently to cause in them some variations, for which no reason can be assigned, and to lead to the preference of practices which are empirical in so far as the trials in the small way differ enough by the rapidity of evaporation, the degree of heat, and the action of the air, to make us cautious of advising changes, whose success has not been verified by operations on the great scale.

We shall select, therefore, in the description of processes, those to which experience, or the name of their authors, appears to give authority; and we shall draw from theory, or even from

\* Grundriss der Farbekunst.

our own trials, such counsels as may guide well-informed artisans in the study and successive improvement of the processes which they employ.

Astringents differ from one another as to the quantity of the principle which enters into combination with the oxyde of iron. Hence the proportion of the sulphate, or of any other salt of iron, and that of the astringents, should vary according to the astringents made use of, and according to their respective quantities. Gall-nut is the substance which contains most astringent; sumach, which seems second to it in this respect, throws down, (decomposes,) however, only half as much sulphate of iron.

The most suitable proportion of sulphate of iron, appears to be that which corresponds to the quantity of the astringent matter, so that the whole iron precipitable by the astringent may be thrown down, and the whole astringent may be taken up in combination with the iron. As it is not possible, however, to arrive at such precision, it is better that the sulphate of iron should predominate, because the astringent, when in excess, counteracts the precipitation of the black colouring particles, and has the property of even dissolving them.

This action of the astringent is such, that if a pattern of black cloth be boiled with gall-nuts it is reducible to grey. An observation of Lewis may thence be explained. If cloth be turned several times through the colouring bath, after it has taken a good black colour, instead of acquiring more body, it is weakened and becomes brownish. Too considerable a quantity of the ingredients produces the same effect; to which the sulphuric acid, set at liberty by the precipitation of the oxyde of iron, contributes.

It is merely the highly oxydized sulphate which is decomposed by the astringent; whence it appears, that the sulphate will produce a different effect according to its state of oxydization, and call for other proportions. It is right, therefore, to follow the advice of Proust, employing it in the oxydized state; but in this case it is only partially decomposed, and another part is brought, by the action of the astringent, into the slightly oxydized sulphate.

The molecules precipitated by the mixture of an astringent and sulphate of iron, have not at first a deep colour; but they *pass to a black* by contact of air, while they are moist.



In these phenomena may be found the reason of two methods which are adopted. 1. Black is not given by a single operation. The dyeing is interrupted and divided into different stages. Thus, the iron which has been de-oxydized, can resume a sufficient quantity of oxygen for the succeeding stage, and the bath which could produce no more effect, acquires anew the property of affording black molecules. 2. The stuffs are aired during the repose of the dyeing; whence the hue of the molecules is deepened.

We stated in the theoretical part, that the black dye was only a very condensed colour, and that it assumed more intensity from the mixture of different colours likewise deep. It is, for this reason, advantageous to unite several astringents, each combination of which produces a different shade. But blue appears the colour most conducive to this effect, and it corrects the tendency to dun which is remarked in the black produced on stuffs by the other astringents.

On this property is founded the practice of giving a blue ground to black cloths, which acquire more beauty and solidity the deeper the blue. Another advantage of this practice, is, to diminish the quantity of sulphuric acid which is necessarily disengaged by the precipitation of the black molecules, and which would not only counteract their fixation, but would further weaken the stuff, and give it harshness.

For common stuffs, a portion of the effect of the blue ground is produced by the *rooting*.

The mixture of logwood with astringents contributes to the beauty of the black in a twofold way. It produces molecules of a hue different from what the astringents do, and particularly blue molecules, with the oxyde of copper, commonly employed in the black dyes; which appears to be more useful, the more acetate the verdigris made use of contains.

The boil of weld, by which the dye of black cloth is frequently finished, may also contribute to its beauty, by the shade peculiar to its combination. It has, moreover, the advantage of giving softness to the stuffs.

The processes that are employed for wool, yield, according to the observation of Lewis, only a rusty black to silk; and cotton is hardly dyed by the processes proper for wool and silk. Let us endeavour to ascertain the conditions which these three varieties of dyeing demand.

Wool has a great tendency to combine with colouring substances; but its physical nature requires its combinations to be made in general at a high temperature. The combination of the black molecules may therefore be directly effected in a bath, in proportion as they form; and if the operation be prolonged by subdividing it, it is only with the view of changing the necessary oxydizement of the sulphate, and augmenting that of the colouring particles themselves.

Silk has little disposition to unite with the black molecules. It seems to be merely by the agency of the tannin, with which it is previously impregnated, that these molecules can fix themselves on it, especially after it has been scoured. For this reason, silk baths should be old, and have the colouring particles accumulated in them, but so feebly suspended as to yield to a weak affinity. Their precipitation is counteracted by the addition of gum, or other mucilaginous substances. The obstacle which might arise from the sulphuric acid set at liberty, is destroyed by iron filings, or other bases. Thus, baths of a very different composition, but with the essential condition of age, may be proper for this dye.

Cotton and linen have a great propensity to combine with the oxyde of iron, so that they withdraw a portion of it even from its solutions in acids. If those processes be considered which are employed in calico printing, and which are capable of guiding us in dyeing cotton and linen, it is apparent that the application of the mordant is the first step, so that the cloth is, first of all, combined with the oxyde of iron; after which it is turned through the dyeing bath.

When black, red, and violet are wished for at the same time, a bath of madder is employed, which affords all these three colours at once, according to the base which fixes the colouring molecules on the different portions of the cloth. The black thereby obtained is, in reality, merely a very deep but durable violet. This is the most ordinary process. If yellows or greys be wished for along with the black, sumach is made use of.

When cloths are to have only black and white colours, a decoction of logwood is employed, which affords a finer and less costly black, but one a little less durable.

We have ascertained, that by imitating these processes, adding a little acetate of copper, making a mixture of different *astringents*, and substituting the pyrolignous for the ordinary

acid, blacks may readily be produced of a satisfactory beauty, whose vivacity is increased at the same time that the harshness derived from the dye is diminished, by means of the oil with which the stuff is impregnated.

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### CHAPTER III.

#### *Of Grey.*

THE shades of black are grey, from the brownest to the lightest. The greys may be made in two modes. 1. A decoction of pounded gall-nuts is prepared, and the sulphate of iron is separately dissolved. A bath is made corresponding to the quantity of stuff, which is to be dyed of the lightest shade; and when it is as hot as the hand can bear, the decoction of nut-galls, and the solution of sulphate are poured into it. The wool or stuff is then turned through it. When it has come to the wished-for shade, it is withdrawn; and some decoction and solution are added to the same bath. A stuff is turned through this, to give it a deeper shade than the preceding. Thus the operation is continued to the brownest shades, always adding more of the two liquors. But it is better for the black-grey, and the other deep shades, to give previously to the stuff a stronger or weaker blue ground.

The second mode of making grey, which Hellot found to be preferable to the one just described, because the decoction of galls takes better on stuffs, and because there is more certainty of employing only the proportion of sulphate of iron required for the shade, consists in boiling for two hours the quantity of nut-galls judged proper, having bruised and enclosed them in a thin linen bag. The stuff is then boiled in this bath for an hour, (*en palliant*,) stirring it up well with the rake, after which it is lifted out. There must now be added to this same bath a little solution of sulphate of iron; and the stuff being turned through it, thus acquires the lightest shade. More solution of iron is to be progressively added, till the deepest hues be produced.

In both of these methods the brownest shades may be begun with, when there is no restraint from patterns, of which the

precise hue is to be hit. In the latter process each piece of stuff is left in, for a longer or shorter time, till it take the wished-for shade.

It is not possible to fix beforehand the dose of the ingredients, the quantity of water, and the time necessary for each of these operations. The eye alone must judge of them. If the bath be strongly charged with colour, the wool need remain a shorter period; but if the bath begins to get exhausted, it will require more time. When the stuff is found to be not dark enough, it is returned a second, a third time, &c.; but if the colour be too deep, it becomes necessary to pass the stuff through a fresh tepid bath, into which a little decoction of galls had been put, or even through a bath of soap or alum. If thus, however, we go beyond the mark, it is requisite to re-brown the stuff. Reiterated operations are prejudicial to it; hence it is proper to attempt to catch the desired shade at once, by withdrawing the cloth occasionally from the bath.

Care must be had that the bath do not boil, and that it be rather tepid than too hot. In whatever manner the greys are dyed, they should be immediately washed in a great body of water; and the brown-greys should be even scoured with soap.

It is frequently desired to mingle with grey the tint of another colour, as a reddish, agate, or hazel cast. In this case, after giving a greater or smaller tint of blue, according to the object proposed, the stuffs are turned through a spent cochineal bath, which has served either for scarlet or violet, adding to it gall-nuts, logwood, madder, &c. Thereafter a browning of greater or less depth is given with solution of iron. For hazel, old fustic and logwood are added to the galls, and the dyeing is given on a white ground. All the greys, except black-grey, are applicable on silk without aluming. The bath is composed with fustet, logwood, archil, and sulphate of iron. These ingredients are varied according to the shade to be given. Thus more archil is employed for greys that are to have a reddish cast; more fustet for those which ought to incline to a russet or green; and lastly, more logwood for such as are to have a darker grey. For the iron-grey, logwood and solution of iron are had recourse to.

The black-grey requires aluming, after which the silks are taken to the river, and then receive a bath of weld. A portion

of this bath is thrown away to substitute for it the extract of logwood. When the silk has been impregnated with this, solution of iron is added in sufficient quantity; and when the desired shade is hit, the silk is washed and wrung.

If the grey come out deeper than is desired, the silk is turned through a solution of tartar, and then through hot water; and if the colour be too much weakened, a fresh dye-bath is given it.

For linen and cotton, a blue ground is given to black-grey, iron-grey, and slate-grey, but not to the other greys. All the shades require a galling proportioned to the grey which is wished to be procured. Baths of nut-galls that had been previously used are often employed.

When the yarn has been galled, wrung, and dried, it is turned over the sticks in a bucket full of cold water, to which a suitable quantity of the black cask,\* and of decoction of logwood, is added. The yarns are worked in it in separate portions, then wrung out, washed, and dried.

Le Pileur d'Apligny gives two other processes for making grey, of which he pretends the dye to be more fixed.

1. The yarn is galled, turned through a very weak *black bath*, and afterwards maddered.

2. The yarn is turned through a very hot solution of tartar, slightly wrung, and dried. This yarn is then dyed in a decoction of logwood. The dye appears black; but on turning through and working the yarn with attention in a hot solution of soap, the surplus of the dye is discharged, and there remains an agreeable and solid slate-grey.

A process, the success of which is known to us, consists in taking a very dilute solution of acetate of iron, (it is sufficient to add a little of this acetate to a quantity of water,) and a decoction of sumach, also very dilute. The cotton is passed in succession from one liquor to the other, till the wished-for shade be attained. The finish is given by passing through a water slightly acidulated by sulphuric acid, otherwise the sumach gives a russet hue. By the same process may be obtained with nut-galls less lively greys; and the alder bark affords an agreeable one, which borders on hazel.

A skilful manufacturer of Rouen has communicated to us the

\* See Part I. p. 227.

following process, which he makes use of successfully for cotton velvets. A galling is given with an equal quantity of gall-nuts and logwood, after which a bath of cold water is administered, and next another bath of water, in which there has been dissolved a weight of sulphate of iron, equal to the one-half of the preceding ingredients. After working the cotton about a quarter of an hour in this bath, it is rinsed in cold water, and brightened.

For this purpose a bath of tepid water is used, to which one-eightieth of decoction of weld, and a little alum, are added. The cotton is left about twenty minutes in this bath, after which it is washed in cold water, and dried.

By modifying the doses of the ingredients, greys from pearl-grey to the deepest grey may be thereby obtained.

For greys on printed goods, the same mordant is impressed as for a clear violet, and sumach or gall-nuts are employed according to the shade that is desired.

## SECTION II.

### OF BLUF.

#### CHAPTER I.

##### *Of Indigo.*

INDIGO is a blue colouring substance extracted from a plant, which is known under the names of *anil*, *indigofera*, and *indigo*.

The plant from which the indigo is obtained, or the *indigofera*, is cultivated in China, Japan, India, Madagascar, Egypt, and South America. There are several species of it; but in America, three are particularly distinguished. The *indigo franc*, or *indigofera tinctoria*, Linn.: it is the smallest, and produces the indigo of the lowest quality; but as it yields a larger quantity, it is often preferred. The second is the *indigofera disperma*, Linn., the species cultivated in Guatemala. It is taller, and more woody than the preceding. It affords a better indigo. The third is the *indigofera argentea*, or bastard indigo, which is still more woody than the last. It furnishes the finest indigo, but in smaller quantities than the others.

It would appear that this plant absorbs more foreign matters the more herbaceous it is. These are afterwards blended with the colouring particles.

When the *indigofera* exhibits the first signs of maturity, it is cut, and carried into vats, where it undergoes a fermentation, to which it is naturally prone. When it is cut down in a state of complete maturity, it affords a finer colour, but in less quantity. If it be cut too late, more of the substance is then lost, and an indigo of worse quality is obtained.

Three vats are placed one over another, at different heights, near a reservoir of water. The first is termed the steeper, (*trem-poir*.) Into this, filled with water to a certain height, the plant is put. Here a very brisk kind of fermentation soon begins, and much froth is thrown up. The gas that is disengaged is partly inflammable.

When the indigo maker ascertains that the fermentation is sufficiently advanced, and that the colouring particles have a tendency to separate, he runs off the liquor into the second vat, which is named the beating-vat, (*batterie*,) in which the liquor is subjected to a beating with instruments constructed on purpose. Le Blond, in some observations which he sent to the Academy of Sciences, says, that this operation is intended for dissipating the carbonic acid generated in the fermentation, which hinders the colouring particles from falling down. He states, that the beating is not sufficient to effect the precipitation of all the colouring particles, and that in French Guyana a process has been tried, which, by causing a more copious precipitation, has revived the hopes of the planters, who had given up this kind of manufacture. It consists in mixing a certain quantity of lime water with the liquor, whereby its carbonic acid is absorbed; but he conceives that the due proportion must not be exceeded, because too much lime water is prejudicial. This method was not unknown. P. Labat makes mention of it. Struve also thought that lime water promoted the precipitation of the indigo, by seizing the carbonic acid which held it in solution.\*

When it is inferred from the blue colour that the beating has been sufficient, the vat is allowed to settle for two hours, that the colouring particles may begin to separate from the liquor, which contains a yellow extractive matter. It is now passed into a third vat, called the *diablotin*, (settling vat.) Here the colouring particles are suffered to subside; and the supernatant liquid is run off, in succession, by two stopcocks placed one above the other; after which the colouring particles themselves, which have a semi-fluid consistence, are drawn off, by a third stopcock, into conical linen strainers. When they are reduced to the consistence of a paste, they are turned out into square boxes, in the open air, which are placed under shades to shelter them from the sun.

The indigo produced in these operations differs not only according to the quality of the plant which afforded it, but also according to the pains taken in the preparation. Its colouring part, however, seems to be an uniform substance. Hence the qualities that distinguish it depend particularly on the propor-

\* Bibliot. médico-physique du Nord, tom. iii.



tion of the foreign parts blended with it, and on the greater or less consistence which it has taken in drying.

There is a light variety, called *light indigo*, or *flower indigo*, which comes from Guatimala, and is of a beautiful blue. It floats on water, whereas the other kinds fall to the bottom of this fluid. It is the finest and the most precious sort. There is another, known under the name of *coppery indigo*, because its surface assumes the colour of copper when it is rubbed with a hard body. Lastly, there are much less pure kinds, as that from Carolina.

The blue molecules of indigo, however, independently of foreign substances, owe a part of their properties to the preparation itself.

When the leaf of indigo is bruised, its juice speedily assumes a blue colour in the air. If, after bruising it, the juice be extracted by infusion, on leaving this solution in the air it grows turbid, and a greenish blue fecula falls down, which preserves this green shade, notwithstanding repeated lotions, and a long exposure to the atmosphere. In Egypt, where the arts have made little progress, the plant is merely bruised, infused in hot water, which is then run off into a pit of argillaceous earth, in which it is agitated with beaters, to cause the precipitation of its fecula; but the indigo thus obtained is always greenish, and affords a bad colour. In this state it seems more disposed to dissolve by means of fermentation; for the dyers require only to mix raw sugar with it, in order to establish the vats which are used for dyeing. A French artisan extracted a fine indigo, by subjecting the plant to the same preparations as in other countries.

The three parts of the process employed, have each a different object. In the first, a fermentation is excited, in which the action of the atmospheric air does not intervene, since an inflammable gas is evolved. There probably results from it some change in the composition of the colouring particles themselves; but especially the separation or destruction of a yellowish substance, which gave to the indigo a greenish tint, and rendered it susceptible of suffering the chemical action of other substances. This species of fermentation passes into a destructive putrefaction, because the indigo, as we shall see, has a composition analogous to that of animal substances.

Hitherto the colouring particles have preserved their liquidity. In the second operation, the action of the air is brought into play, which by combining with the colouring particles, deprives them of their solubility, and gives them the blue colour. The beating serves, at the same time, to dissipate the carbonic acid formed in the first operation, whose action is an obstacle to the combination of the oxygen. The separation of this acid is promoted by the addition of the lime; but if a redundant quantity be introduced, the excess would act upon the indigo and counteract the free combination of the oxygen.

The third part of the process has for its objects the deposition of the colouring part, become insoluble by combination with oxygen; its separation from foreign substances; and its desiccation, which gives it more or less hardness, whence its appearance varies.

Indigo is not only of very extensive use in dyeing, but its chemical properties are very remarkable. They explain, in a clear and positive manner, those processes of dyeing, in which they are used; they point out interesting analogies with other phenomena. For these reasons, we shall present, at some detail, the observations of the chemists who established this theory. We owe it especially to Bergmann.

In the experiments of this great chemist,\* water dissolved, by means of ebullition, a ninth part of the weight of the indigo. The portion dissolved by the water appeared partly astringent, partly mucilaginous, and partly saponaceous. The solution of alum, and of sulphate of iron and copper, precipitated its astringent parts.

Quatremere† also separated by means of water the parts which are soluble. He states their quantity to be more considerable, the worse the quality of the indigo; and that, after this operation, the residuum has acquired the qualities of the finest indigo. He therefore proposes to purify what is of inferior quality, by boiling it in a bag, and renewing the water till it ceases to acquire colour. This operation would undoubtedly be beneficial, since the indigo would thereby be deprived of the

\* Analyse et examen chimique de l'indigo. Mem. des Savans etrang. tom. ix. Opusc. tom. v.

† Analyse et examen chimique de l'indigo, tel qu'il est dans le commerce, pour l'usage de la teinture. Mem. des Savans etrang. tom. ix.

yellowish particles which may alter its colour. Yet there are probably differences in the nature of the colouring particles themselves, and in the insoluble earthy matters, which could not in fact injure the colour, but might change the proportions of the colouring particles.

The powder of indigo, digested in alcohol, gave at first a yellow tincture, then red, and lastly brown. It lost, by this operation, repeated several times, about one-seventeenth of its weight. Water separates from this tincture a brownish resinous matter.

Ether acts on indigo nearly like alcohol; but the oils, both fixed and volatile, have little action on it.

Bergmann mixed one part of indigo, well pulverized, with eight parts of colourless sulphuric acid, of specific gravity 1.90. The glass bottle in which the mixture was made was slightly corked. The acid speedily attacked the indigo, and excited a great heat. After a digestion of 24 hours, the indigo was dissolved; but the mixture was opaque and black. On adding water it cleared up, exhibiting successively all the shades of blue, according to the quantity of water. It requires, at least, 22 pounds of water in a cylindrical glass vessel, of  $7\frac{1}{2}$  inches diameter, to render the smallest drop of this solution imperceptible.

If sulphuric acid be diluted with water, it attacks only the earthy matter that is blended with the indigo, and some mucilaginous ingredients.

Several goblets in which a drop of this solution was mixed with liquids, which contained different substances, such as acids, alkalies, neutral salts, were exposed for some time to a temperature of  $15^{\circ}$  or  $20^{\circ}$  R., ( $66^{\circ}$  or  $77^{\circ}$  Fahr.) In some the colour was preserved without alteration; in others it became green, and was destroyed more or less speedily. Bergmann explains the changes which he observed, by the property which some substances possess of carrying off phlogiston and others of giving it. They are happily explained by the affinities of oxygen, which some substances afford, carry off, or absorb from the atmosphere.

The fixed alkalies, saturated with carbonic acid, separate from the solution of indigo a very fine blue powder, which is very slowly deposited. Bergmann distinguishes this blue powder by the name of *precipitated indigo*. It is also obtained by pouring, drop by drop, the alcoholic solution into saturated

solutions of alum, of sulphate of soda, or of some other salts which contain sulphuric acid; but the liquid remains always a little coloured.

Muriatic acid digested, or even boiled with indigo, takes up the earthy part, the iron, and a little extractive matter, which colours it yellowish brown, but without attacking in any manner the blue colour. If indigo be precipitated from sulphuric acid in this case, muriatic acid dissolves very easily a certain quantity of it, and forms a deep blue liquid.

The other acids, as the tartaric, formic, acetic, and phosphoric, comport themselves with indigo like muriatic acid. They dissolve precipitated indigo very well. Sulphuric acid, when too much diluted with water for dissolving indigo, and nitric acid, also too weak for decomposing indigo, only dissolve the earthy portion and the extractive matter, which are foreign to the colouring substance.

Concentrated nitric acid attacks indigo with such violence as to inflame it. If it be weakened to a due degree, it acts with less vivacity. The colour of the indigo becomes ferruginous, (ochrey.) The residuum, after this operation, has the appearance of the earth of umber, and forms in weight only one-third of the indigo. The fixed alkali precipitates a little oxyde of iron, mixed with barytes and calcareous earth, from the nitric acid which has acted on the indigo; but if too much alkali be added, a portion of the precipitate is re-dissolved, rendering the colour of the liquor deeper than it was before.

Haussman, in a very interesting dissertation, describes a connected series of observations on the changes which nitric acid produces on indigo.\* When the whole indigo seemed destroyed, there was found a coagulum, which, after being deprived of all the nitric acid by washing, formed a brown and viscous mass, which dissolved in alcohol, and was soluble only in a great quantity of water. It possessed considerable bitterness. The water which has served for the lotions, afforded by evaporation small crystals, which were probably oxalic acid.

Chlorine has little action on indigo in substance. But this inaction depends only on its cohesion, for it easily destroys the colour, and changes the composition of indigo when in solution.

\* Journ. de physique, 1788.

If the liquid be evaporated after this destruction is effected, there is found a blackish substance analogous to what results from the decomposition by nitric acid.

The decomposition by nitric acid and by chlorine is reciprocal, and the effects depend on the passage of the oxygen of one of these acids, into a more intimate combination with the hydrogen and carbon, especially with the hydrogen. A combination is formed in which the carbon predominates, but in proportions determined by circumstances.

Sulphuric acid is, therefore, the only one which dissolves indigo; but we shall see that it produces this effect only by means of a change of composition, which alters very little the colour of the indigo, but renders it soluble in the other acids and the alkalies.

Fixed alkali dissolves some substances distinct from the colouring part of indigo; but it attacks slightly the colouring particles themselves. Ammonia, or the caustic volatile alkali, acts nearly in the same manner. Precipitated indigo dissolves readily, and in the cold, in the alkalies, whether fixed or volatile, if they be pure or caustic. Their blue colour changes gradually to green, and is eventually destroyed. But if the alkalies be combined with carbonic acid, they do not produce this effect. Lime water has little action on indigo, but it dissolves what has been precipitated. It alters and finally destroys its colour, nearly like the caustic alkalies.

Indigo exposed to the action of fire in an open crucible, or under a muffle, smokes, swells up, reddens, and sometimes even takes fire, evolving a white flame. One hundred parts of indigo leave thirty-three or thirty-four parts of ashes.

These ashes do not afford fixed alkali, when they are lixiviated with distilled water. Muriatic acid dissolves the greater part of them with effervescence. The residuum, which is insoluble, forms an eleventh part, and has the characters of siliceous earth.

The solution made in muriatic acid produces prussian blue, on mixing it with prussiate of potash; but the iron thereby separated is not to be confounded with that which enters only into the colouring particles.

Besides iron and siliceous earth, the ashes contain calcareous earth and barytes.

Indigo detonates strongly with nitre. It afforded by distil-

lation carbonic acid, a liquor which contained a little volatile alkali, and an oil similar to the empyreumatic oil of tobacco, which dissolved very well in alcohol.

Bergmann concludes from his analysis, that 100 parts of good indigo contain—

Mucilaginous parts separable by water . . . . .	12
Resinous parts soluble in alcohol . . . . .	6
Earthy parts soluble in acetic acid, which does not attack the iron here in the state of an oxyde . . . . .	22
Oxyde of iron dissolved by muriatic acid . . . . .	13
47 parts remain, which are colouring molecules almost pure, and which when distilled afforded—	
Carbonic acid . . . . .	2
Alkaline liquor . . . . .	8
Empyreumatic oil . . . . .	9
Charcoal . . . . .	23

The charcoal, when burned in the open air, yielded four parts of earth, of which about one-half was oxyde of iron, and the remainder a very subtile siliceous powder.

It results from this analysis, that pure indigo contains nearly the same elements as animal substances, and it is to be supposed that some phosphate will be discovered in the ashes; but what distinguishes it from animal bodies, is the large quantity of charcoal which must give to its composition a greater stability than ordinary animal substances possess. We have, however, already seen that if its preparations have not been made with skill, it might experience the effects of putrefaction. It is thereby altered or destroyed. That whose fermentation is pushed too far becomes black; it is termed *burned indigo*. (NOTE GG.)

Bergmann ascribes its colour to iron, comparing it to the prussiate of iron, and to the black molecules formed by the combination of an astringent with the oxyde of iron. This comparison does not appear to us exact. The iron present in the colouring particles of indigo, constitutes seldom more than the thirtieth part of their weight. The modifications which they receive from the combination of oxygen, or its expulsion, which we shall presently examine, do not correspond to the effects of the oxydation of this metal. It seems therefore more

proper to consider the colour of indigo as a result of the reciprocal action of all its elements, than as a property derived from one of them.

It has been seen that the alkalies and lime do not dissolve indigo; but in the processes made use of, it becomes soluble in these substances, from which it is afterwards precipitated on the matters that are dyed. The solution of indigo in alkali or lime is greenish; it becomes blue at its surface, because the indigo is precipitated from it under its natural form. Bergmann remarks, that this green colour is not produced by the alkalies, as happens with several other vegetable substances. For these blue parts which have become green, recover their colour whenever the alkali is saturated with an acid, which itself would give them a red colour. But the particles of the indigo must have undergone a change, so as to become soluble in the alkalies; and the acids have not the property of making them red. Our object is now to examine what change the particles of indigo suffer in order to be dissolved in the alkalies.

Bergmann examines two processes, with the view of ascertaining the cause of the changes experienced by indigo. We shall enter into further details on these processes, when we come to examine them as dyeing operations. It is enough at present to indicate them. If sulphate of iron, dissolved in water, be mixed with its own weight of indigo, and double its weight of lime, the indigo is soon dissolved. But Bergmann has observed, that if the sulphate of iron be kept boiling in a great deal of water for several hours, and if this water be reduced by evaporation to a proper quantity, the solution can no longer take place. If to a solution of pure or caustic fixed alkali, indigo and sulphuret of arsenic or orpiment be added, the bath soon becomes green, and the solution of indigo is accomplished. If, for the sulphuret of arsenic, be substituted the proportion of arsenic which it contains, the bath will never be fit for dyeing; but on adding to it the proper quantity of sulphur, symptoms of solution will soon be seen.

Bergmann ascribed these effects to the phlogiston communicated to the indigo, in the first case, by the precipitate of iron; and in the second, by the sulphuret of arsenic, through the agency of which it has become soluble in the alkali and lime. Hence, when the precipitate of iron has been deprived of its

phlogiston by a long ebullition, it ceases to be able to dissolve indigo.

For this hypothesis, which might enable us sufficiently to foresee the results, we have merely to substitute the explanation founded on the positive effects of oxydation and deoxydation.

When indigo has assumed a blue colour, it contains a certain proportion of oxygen, which renders it insoluble. It may be compared to a metal, which, at a certain degree of oxydation, becomes insoluble in the acids, and which resumes its insolubility by the action of substances which can diminish its oxydation. Indigo is rendered soluble by the substances which can deprive it of a variable quantity of this element. The recent precipitate of sulphate of iron attracts oxygen powerfully from the atmospheric air, as Priestley has shown. It must exercise a similar action on indigo, and render it soluble. When the alkali acts on the sulphuret of arsenic, it precipitates from it the arsenic which is in the metallic state, robbing it of a portion of its oxygen. In this case, it acts on oxygen like the precipitate of iron, and in the same way renders the indigo soluble; but the co-operation of the oxydable metal is required. Oxyde of arsenic produces no effect.

The deoxydation, however, would not alone suffice, nor would it give a great enough solubility in water. The action of a substance possessing the property of uniting with the deoxydized indigo, and increasing its solubility, must be joined, in order to prepare it for dyeing. This is the function of the fixed alkalies and the lime, in the different processes employed. It results from this twofold action, that, on one hand, the indigo is deoxydized, while, on the other, it enters into a liquid combination with the alkali or the lime.

That this double action is essential, is evident; because the sulphuret of potash, or of soda, does not effect the solution of indigo, although it strongly attracts the oxygen, in order to be converted into a sulphate. The incompetency of its action must be ascribed especially to the resistance offered by the cohesive force of the indigo.

Some experiments of Haussman serve to confirm this theory. He put a solution of indigo, made by means of alkali and orpiment, in contact with the gas extracted from nitre by distilla-



tion with heat, which is oxygen gas with a small proportion of azote. The whole of the oxygen was absorbed, while the indigo separated, resuming its blue colour, and the insolubility belonging to it in this state. The metal was reduced to an oxyde. The sulphur formed a sulphate with the alkali, and the excess of the alkali could not retain in solution the indigo restored to its natural condition.\*

To Haussman we owe several other interesting observations.

The sulphuret of antimony determines the solution of indigo equally with the sulphuret of arsenic; but this solution cannot be employed like that of the sulphuret of arsenic, because the metal forms a red precipitate, which is probably a sulphuretted oxyde of antimony. This oxyde, mixed with the sulphur, does not produce solution. Iron, in the metallic state, put into a concentrated alkaline liquor, along with indigo ground in water, did not, any more than zinc, determine its solution. Their force of cohesion, undoubtedly, counteracts this effect, while antimony, in the metallic state, was able to occasion the solution.

The precipitate of copper, far from contributing to the solution of indigo, produced a contrary effect. It caused its regeneration in solutions made by means of sulphuret of arsenic or of antimony, as well as in that occasioned by the precipitate of iron. The solution of copper in ammonia acted in the same way. Haussman says, that the dyers take advantage of this property of copper, to exhaust more speedily the blue vats, which, when they have served too long, or are naturally little loaded with indigo, would furnish only very weak shades; while deeper ones are obtained by passing the pieces, before dyeing them, through a water slightly impregnated with sulphate of copper, or other cupreous solution, acid or alkaline. But the dyers of whom he speaks are in a mistake. When a solution of copper is poured into a transparent solution of indigo; the latter becomes of a deep blue, and the regenerated indigo is precipitated. In like manner, cloth impregnated with a solution of

\* All the effects which we explain by the oxydation and deoxydation of the indigo, might be accounted for by supposing that the indigo is rendered soluble by an excess of hydrogen, and that the means which restore it to its blue colour, carry off from it this hydrogen. But this second explanation requires the admission of decompositions of water by causes of small energy, and it is not supported by the analogy of the oxydations of the metals, sulphur, phosphorus, &c. Hence, the one we adopt appears to have at least much more probability.

copper, on being plunged into a vat, comes out of it instantly of a deep blue, but washing removes this completely. This is, therefore, a means of quickly exhausting the vats, to the detriment of what the stuffs could take from it; for the regenerated indigo contracts no union with them. We shall see, that advantage is taken of this property of copper, to reserve (protect) the parts of a stuff in an indigo bath.

The oxyde of copper produces these effects by the facility with which it gives up its oxygen to indigo that has been deprived of it. The oxyde of tin, which has a contrary disposition, ought to act differently.

Bancroft found that tin, slightly oxydized, when mixed with an alkaline solution of indigo, speedily effected a solution of the latter, thereby forming, as is said, a good vat.

Tin, oxydized with a strong heat, or by the detonation of nitre, not only did not effect the solution of indigo, but it even counteracted it, on being mixed with the sulphuret of arsenic or antimony, or the precipitate of iron, so that in this state it gave up a portion of its oxygen.

Tin, slightly oxydized, may be dissolved directly in potash, and this solution acts on indigo. It quickly produces a vat, in which cloths are dyed of a very intense blue.

In all the processes employed for establishing the solutions of indigo, called *vats*, which we shall describe, there is present, conformably to the theory, several substances which, by an action more or less slow, serve to carry off the oxygen, while the lime, fixed alkali, or even the ammonia, unite to the deoxydized indigo, and give it more solubility.

It appears that indigo passes by these means through different degrees of deoxydation, so that its solution assumes different shades. In the most advanced state its solution is colourless; with less oxydation it passes to a yellow, and finally to a greenish hue.

While indigo is in solution, the portion of it in contact with the air absorbs oxygen, which combines with the indigo, and regenerates it, saturating, at the same time, the substance which tended to seize it, so that the surface becomes blue. Thence the froth, green at first, and then blue, is called *fleurée*, which is formed in well constituted vats, when they are agitated.

Indigo, when in the liquid state, easily forms combinations.

It then unites to stuffs, and abandons the alkalies, which have but a feeble action on it. Notwithstanding the more intimate combination which it thus forms, it attracts oxygen, when the stuff is exposed to the contact of air, so that from yellow or green it passes speedily to blue. The same effect is produced, if on coming out of the bath it be dipped in very weak chlorine solution. It thereby appears, that if cloth cannot combine directly with indigo, it is only in consequence of the counteracting force of cohesion.

Some vats are prepared and used in the cold, others are employed hot. The same difference is remarked here, in reference to stuffs, as in the most part of other dyes. Wool combines with a great deal of indigo. Its combination is very durable, but it requires heat, which disposes it to be formed. Silk takes a deep blue with more difficulty. Cold vats are proper for cotton and linen.

When indigo is dissolved by sulphuric acid, it gives a lively colour to stuffs. We shall examine this process; but the colour is much less solid than that produced by the ordinary vats; and we have seen, by the experiments of Bergmann, that the precipitate obtained from this solution is different in some of its properties from native indigo, and that it is soluble in the other acids, and in the alkalies. The indigo must therefore have suffered some alteration in its composition.

It would seem that the observations which have been made on sugar, and other vegetable and animal substances,\* may be applied to the action of sulphuric acid on indigo, and that it determines the formation of a little water, by the intimate combination of a portion of the oxygen and the hydrogen, which enter into the composition of the indigo. Thus, we may explain the great heat which is produced without any sulphurous acid being formed, the state of concentration in which the sulphuric acid must be, and why other acids, although powerful and concentrated, cannot effect this solution.

This alteration is, in our opinion, capable of being formed in different degrees; and when the heat has been rightly tempered, we hardly find in it the properties described by Bergmann, whose accuracy cannot be called in question.

\* *Essai de statique chimie*, tom. iv. p. 530.

If sulphuretted hydrogen water be poured into a solution of indigo, diluted with so much water that it has but a faint colour, this is soon seen to disappear, and a little chlorine restores it.

A hydrosulphuret produces this effect with a much more concentrated solution. If cotton be immersed in the liquid, it comes out colourless, but soon becomes green, and then passes to blue. A deep colour may be given to it by this means. Here the indigo did not offer any obstacle by its cohesive force; and the sulphuretted hydrogen, which is condensed, acts powerfully upon it.

The observations made by Bergmann, on the effects that different substances produce on solution of indigo in sulphuric acid, are all easily explained by the property which they may or may not have of seizing its oxygen.

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## CHAPTER II.

### *Of Pastel and Wood.*

PASTEL is a plant of the cruciform family, whose distinctive character is derived from the form of its silique, which is flattened like the fruit of the ash, is edged with a thin membrane, and contains two oblong seeds. Two species of it are distinguished, of which there are varieties; the cultivated pastel, *isatis tinctoria*, Linn., and the pastel of Portugal, *isatis lusitana*, Linn., which differs from the first in being smaller, and in having narrower leaves. The first species sends out stems a metre high, (a yard,) of the thickness of the finger, which are divided into a number of branches, loaded with many large leaves, which are lanceolate, furnished at their edges with small smooth indentations, and of bluish-green colour. The flowers are yellow, disposed in panicles at the summits of the stems. The root is thick, woody, and penetrates deeply into the earth.

This plant requires a good black mould, light, and well improved. It is sown in spring, after a double tillage in autumn. Three or four crops are obtained in a year. The first when the stems begin to grow yellow, and the flowers are about to appear; the others at successive intervals of six weeks or more, according to the climate and heat of the season.

The plant is mown with a scythe, washed in the river, and dried in the sun. Its desiccation must be rapidly performed; as, if the season be unfavourable, or if it rains, the plant runs a risk of being spoiled. A single night is sometimes sufficient to turn it black.

The plant is thereafter carried to the mill to be ground and reduced into a paste. This is formed into heaps, which must be covered to protect them from the rain. After fifteen days the pastel mass is opened up and bruised, mixing the interior with the crust that has formed upon its surface. It is then formed into balls, which are carried into a place exposed to the wind and the sun, in order to expel the humidity which might cause them to putrefy. These balls, piled one over another, become hot imperceptibly, and exhale an odour of ammonia, which is stronger in proportion as the quantity is larger, and the season more hot. The heat thus begun, is increased by a slight sprinkling of water, till the pastel be reduced to a fine powder. It is now in the state in which it is found in commerce.

Pastel is cultivated and prepared in several parts of France. That of the southern departments is most esteemed. The name of *vouède* (woad) is given it, in the departments of the north. Woad differs from ordinary pastel, merely in requiring a larger quantity of it to produce a like effect, as Hellot has proved.

Pastel affords, without indigo, a blue colour which has no brilliancy, but is very durable. As it yields much less colouring matter than indigo, and as its colour is inferior in beauty, the discovery of indigo has considerably diminished the culture and sale of pastel.

Astruc relates, in his memoirs on the natural history of Languedoc, that having treated pastel in the small way as the anil is treated to obtain its indigo, he procured a powder which produced the same effects as indigo. Hellot thence concluded, that the deep green of several plants is owing to yellow and blue particles, and that, if by fermentation the yellow could be destroyed the blue would remain. But Lewis says,\* that having made different species of plants putrefy in water, he obtained no blue fecula. This mixture of blue and yellow molecules to form

\* The chemical works of Gaspar Neumann, by William Lewis.

the green of plants, is a supposition void of foundation. But some plants of different species appear to contain likewise colouring molecules analogous to indigo; and the pulp of the fruit of the *genippa Americana*, *Linn.*, contains enough of it, according to Bancroft, for dyeing directly a deep blue—a circumstance already mentioned.

Several attempts have been made in different places to extract an indigo from pastel. It appears that the product is too small, for the colouring substance to enter into competition with ordinary indigo.

In some parts of Africa, they content themselves with giving the leaves of indigo a preparation similar to what pastel is subjected to; but for extracting the blue fecula of pastel, they imitate the preparation of indigo. We shall now give a description of the operations followed in a manufactory, according to the account of it published by Gren.\* The fresh leaves of pastel are taken, which are washed, to separate the impurities and the earth, in a tub of an oblong form, nearly three-fourths full. To prevent the water from buoying them up, pieces of wood are fixed across. On these leaves enough of pure water is poured to cover them entirely, and the vessel is set in a moderate heat. There is formed, according to the temperature of the atmosphere, in a longer or shorter time, a copious froth on the surface of the water, which indicates the commencement of the fermentation. The surface becomes wholly covered by degrees with a blue skin, which presents to the eye shades of copper colour. Whenever there is a certain quantity of this froth, the liquor, which is of a deep green tint, is drawn off into another oblong vat by a stopcock placed immediately above its bottom, or otherwise the water is ladled out to put it into the other vat. In both cases it is necessary to run the water through a cloth into the other vessel, in order to separate the impurities, or the fragments of leaves which might pass over. The leaves are washed with a little cold water, to detach the portions of coloured skin which may adhere to them; and this washing is mixed with what had been drawn off. When this is done, lime water is poured into the liquor of the fermented pastel, in the proportion of two or three pounds for every ten pounds of

\* Crell; *Neueste Entdeckungen*. A translation of it is to be found in the *Bibliothèque médico-physique du Nord*, tom. iii.

leaves, and the mixture is strongly agitated for some time, to facilitate the separation of the indigo, which falls down on repose. To ascertain if the agitation has been continued long enough, a portion of the clear yellowish liquor is put into a common bottle, on shaking which, it will be seen whether blue be still separated, and in this case the liquor must be agitated anew. When the whole of the indigo is finally separated and deposited, the clear water is drawn off by a stopcock, placed at some distance above the bottom of the tub, or by means of a syphon, which ought to be done without loss of time. In order to facilitate the separation of the water, the tub may be inclined to the side of the stopcock, as soon as the stirring is over. The blue colour which remains is poured into conical filters of linen cloth, or into large filtering bags, (*chausses d'Hippocrate*,) Hippocrates's sleeves. But as, at the beginning, a little colour always passes over, it should be received in a vessel placed beneath, and returned into the filter till the water comes off clear. The indigo contained in the filters isedulcorated with a sufficient quantity of water, and dried in the shade, or by a gentle artificial heat, taking care to cover it up.

The indigo may be procured without the addition of the lime water, but much less abundantly. If a larger quantity of lime water be added, the amount of indigo is indeed greater, but it is of inferior quality; because the surplus of the calcareous earth unites to the indigo. The alkaline salts, likewise, facilitate this separation of the blue colour; but it is not advantageous to employ them, because they afterwards dissolve a portion of it. With the addition of an acid, no precipitate takes place.

A certain time must elapse before it is proper to draw off the water which has fermented with the pastel leaves. If it be run off too soon, but little indigo is obtained; if, on the contrary, the leaves be left too long in infusion with the water, they enter easily into putrefaction, diffusing a fetid and peculiar volatile odour. Thenceforth no more precipitate can be separated, and the water remains permanently green. The same thing happens with the water drawn off, if it be neglected; and, even when the indigo is already separated from the liquor, care should be taken that this do not putrefy, otherwise the indigo will be entirely, or at least partially spoiled.

We must not, however, be too hasty in turning the water

into the vat in which it is to be agitated, on the first appearance of the skin of changing blue, (*peau bleue chatoyante*,) since it is at this moment that the water takes up most indigo.

When the degree of the atmospheric heat is considerable, the fermentation is very speedily established, and fifteen or eighteen hours may be sufficient. It is especially requisite, then, to be very attentive, not to let it run into total putrefaction. If the heat of the atmosphere be too low, neither much froth, nor blue pellicle, is to be perceived, but the liquor inclines gradually to putrefaction, without presenting any marked phenomena before its commencement.

The plants piled up, or their juices, enter more rapidly into fermentation, but they afford only a dirty blue.

The indigo extracted from the pastel must be dried in the shade, because the sun destroys its colour.

D'Ambourney, who seems to have had no knowledge of the preceding experiments, was also occupied with the means of forming indigo from pastel.\* He succeeded by letting the fresh leaves of pastel ferment in a certain quantity of water; he took out the leaves, and poured solution of caustic alkali into the liquor, after which he filtered it. A fecula remained on the filter, which he compared to the indigo of Carolina. The fresh and ripe leaves afforded 1-70th of fecula. (NOTE HH.)

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### CHAPTER III.

#### *Of Dyeing Blue with the Indigo and Pastel Vat.*

DIFFERENT processes are employed for dyeing blue by means of indigo. We shall take a survey of these processes, without entering into the details, which are well known in the dye-house, and which are to be found described with much care in the work of Hellot.

The preparation for dyeing blue is not made in boilers, as for the other colours, but in large wooden vessels, to which the name *vats* is given. The vats are let down into the ground, so as to rise above it only to a man's standing height. As it is

\* *Supplement au recueil des procédés d'expériences, &c.*



important to maintain the heat of the vats, they are not put in the same place with the boilers, for which a free circulation of air is needed, but in an adjoining apartment, constructed in a manner adapted to preserve the heat. The name of *guesdres* is given to this arrangement, and the workmen are called *guesdrons*, who should be skilled by long experience to prevent the accidents to which the vats are liable.

Blue may be dyed with pastel or woad. A durable blue would be made, but it would not be deep, and only a small quantity of colour would be obtained, as has been said in treating of these substances. But by mixing them with indigo, vats are formed, very rich in colour, which are almost the only ones in use for wool and woollen stuffs. They are distinguished by the name of pastel vats.

Hellot has not designated with precision the proportion of the substances which are employed in the pastel vat. We shall borrow from the memoir of Quatremere the description of a vat of this kind. It is, however, to be remarked, that the quantities vary, not only in the different dye-houses, but also according to the shades wished to be obtained.

For a vat which is nearly 8 feet in depth, and 5 feet in diameter, two bales of pastel are thrown into the bottom, weighing together 440 pounds, but they are previously broken down.

Thirty-three pounds of weld are to be boiled in a copper for three hours, in a quantity of water sufficient to fill the vat. When this decoction is made, 33 pounds of madder are added to it, and a basket of bran. The mixture is boiled for half an hour longer, and then refreshed (cooled) with 70 gallons of water. The bath is left to settle; the weld is withdrawn; this bath is transferred into the vat; and this is finally stirred up with a rake during the whole period of the transvason, and even a quarter of an hour longer.

All these operations being over, the vat is covered up very warmly, and left six hours in this state, after which it is uncovered, and raked during half an hour. The same thing is repeated every three hours.

When blue veins are perceived on the surface of the vat, its *ground*, (*pie'd*.) as it is called, is given; that is to say, 8 pounds of quicklime. Whenever this substance is introduced, new characters make their appearance. The colour of the vat be-

comes of a blacker and deeper blue, and its exhalations grow much more acrid.

Immediately after introducing the lime, or at the same time, the indigo is put into the vat, after having ground it in a mill with the smallest possible quantity of water. When it has been diluted into the consistence of a thick pap, it is drawn off through a stopcock placed at the lower part of the mill, and it is thrown, without any other preparation, into the vat. The quantity of indigo which must be put into a vat, is determined by the shade to which the cloth or wool is to be brought. For a vat composed in the above proportions, from 11 to 33 pounds of indigo may be employed without inconvenience.

When, on striking the vat with the rake, a beautiful blue froth called *fleurée* is obtained, nothing more is needed previous to dyeing, except to work with the rake twice in the space of six hours, so as to mingle the materials perfectly. It is sometimes necessary to add also a little lime.

The bath, when first poured on the pastel, was boiling hot; and care must be taken not to leave the vat exposed to the open air longer than is necessary for raking. As soon as that operation is finished, the opening is closed by a large wooden lid, on which thick coverings are spread; and every method is had recourse to for keeping up the heat of the vat without the intervention of fire. But notwithstanding these precautions, however favoured by the arrangement of the *guesdres*, the heat can be kept up for only a certain time. At the end of eight or ten days it is found to be much reduced, and would be entirely dissipated if the liquor were not heated again.

This operation consists in transferring the greater part of the vat bath into the boiler, under which a strong fire is kindled. When this bath has received a sufficient heat, it is turned back into the vat in the same manner, and again covered with care.

The pastel vat is liable chiefly to two accidents: the first occurs when it gets stiff or thrown back, according to the language of the vat-men. This accident is perceived, when, on uncovering a vat which had already afforded fine blue shades, it is found to be black, without any appearance of blue veins, and without *fleurée*, (*froth*.) If it be raked up, only a black colour, more or less deep, is remarked: and the odour of the bath, instead of having in it something sweetish, as when the vat is in good

condition, affects the nose, on the contrary, in a very pungent manner. If dyeing be attempted in a vat exhibiting these characters, the stuff takes no colour, or only a dirty grey. These bad qualities depend on an excess of lime; and Quatremere states, that he has communicated them to a vat by overdosing it with lime.

The vat-men employ different means to restore a repelled vat. Some put tartar into it, others bran, urine, madder; and others content themselves with re-heating it. According to Hellot, the best remedy is to put into it bran and madder at discretion; and if it be only a little too much dosed with lime, it is sufficient to let it rest five or six hours at farthest, putting into it only a certain quantity of bran, and three or four pounds of madder, which are diffused through the vat. If it be thrown back to the degree of affording blue, only when it is cold, it must be allowed to recover without disturbing it, and sometimes be left whole days without being stirred with a rake. When it begins to make a tolerable pattern, the bath must be re-heated, in which case the fermentation usually revives. It may be excited with bran and madder, and even with a basket or two of fresh pastel.

Hecquet d'Orval and Ribacourt advise to rest satisfied without raking up, if the bath be but slightly thrown back; but if the evil has made more progress, to put into it some pounds of bran enclosed in a bag, and to diffuse through it at the same time three or four pounds of tartar in powder. The bag, after five or six hours, begins to float and is withdrawn, and the rake is used. If the vat be not yet restored, the same operation is repeated.

Quatremere says, that he has re-established a vat which he had thrown back by an excess of lime; and that for this effect he contented himself with heating twice, and leaving it then in repose for two days, after which it afforded a well characterized *fleurée*. He left it again in repose for three days; and lastly, heating it for the third time, he found it to be restored.

The second accident to which the pastel vat is subject, is putrefaction. When this accident occurs, the veins and the *fleurée* disappear, its colour becomes russet, (*rousse*,) the paste which is at the bottom rises up, the smell becomes fetid.

Quatremere asserts, that if a pattern of a dark blue be

plunged into a vat thus deteriorated, its colour becomes several shades lighter. Putrefaction takes place in a vat, because it has not been sufficiently furnished with lime. Whenever the marks of putrefaction appear, we must hasten to correct it, by adding lime and raking up. This operation is reiterated till the vat be restored; but we must beware of passing to the opposite excess.

It appears, that a just distribution of lime is the object which demands most attention in the conduct of a pastel vat. It moderates the fermentation of the pastel, and of the other substances that serve to de-oxydise the indigo; for this effect, pushed too far, destroys the colouring particles. But too strong an action of the lime becomes too great an obstacle. It is therefore proper to wait till the excess of lime disappears, undoubtedly by the successive formation of carbonic acid, or the source of the fermentation must be increased, or a portion of the lime be saturated by a vegetable acid. Another use of the lime is to hold in solution the colouring particles of indigo and of the pastel, which are de-oxydised. Woad is employed as well as pastel, but it appears that the preliminary preparation which both are subjected to, is not essential. We have seen a skilful dyer of Rouen employ for his vat the plant of woad simply dried; and assert that he derived more advantage from it than from ordinary woad.

The vat is raked up two hours before dyeing; and to prevent the sediment which settles at the bottom, and which is called paste, from producing inequalities in the colour, there is introduced into the vat a species of trellis (lattice work) formed of thick ropes, which is called *champagne*; and when wool is to be dyed in the fleece, there is even placed over the lattice a net with close meshes. The wools or stuffs are to be well moistened in clear water somewhat hot; they are to be squeezed and then plunged into the vat, where they are moved about longer or shorter, according as a colour of greater or less depth is wanted, airing them from time to time. The green colour which the bath communicates, changes into blue by the action of the air. It is difficult to give an equable light blue tone in a rich bath. The best method of obtaining these shades, is to use vats which are already exhausted and beginning to cool.

Wools and stuffs dyed blue ought to be washed with much care, to carry off the particles that are not fixed on the wool; and even the stuffs which are of a somewhat deep blue ought to

be cleansed carefully at the fulling-mill, with a little soap, which does not affect the colour. Those intended to be dyed black must be treated in the same way; but this operation is less necessary for such as are to be turned green.

The name of *indigo vat* (*cuve d'Inde*) is given to the vat into which no pastel or woad enters. The vessel which serves for this operation\* is a boiler, which, by its conical form, leaves between it and the masonry which surrounds it, and on which its brim rests, a sufficient vacuity for introducing a fire. Into this copper are poured 140 gallons of water, more or less, according to its capacity. In this are dissolved  $6\frac{1}{2}$  pounds of *cendres gravelées*, (alkaline ashes of the vine,) as much bran, and 13 ounces of madder, which are all made to boil. Into the vats, even the sediments of these materials are put. There is now poured in  $6\frac{1}{2}$  pounds of indigo ground with water. Careful raking follows. The vat is shut up; a slow fire is placed round it; a second raking is given 12 hours after it is mounted, and thus in succession, from 12 hours to 12 hours, till it has come to blue, which will take place at the end of 48 hours. If well managed, the bath will be of a fine green, covered with coppery flakes and scum, or blue *fleurée*.

This vat is much easier to conduct than that of pastel; but as its whole blue is derived from indigo, it is dearer. The alkali which serves as solvent being more soluble than lime, the dyeing bath is much richer in colour; lastly, the cloths retain more softness in it, than in the pastel vat, where lime is the solvent. When the above vat is in the suitable state, it is employed for dyeing in the manner which has been indicated for the pastel one.

Hellot describes two vats in which indigo is dissolved by means of urine. Madder is added, and to one, vinegar, and to the other tartar and alum, each equal in weight to the indigo. The quantity of urine should be considerable. The solution of indigo, deprived of its oxygen by urine and madder in fermentation, is due to the ammonia formed in the urine, either by the action of heat or fermentation. Hellot remarks, that an effervescence occurs when the solution of alum and tartar are poured in, substances which serve probably to hinder the progress of

\* Mémoire sur l'indigo, par Hecquet, d'Orval et Ribacourt.

putrefaction. But these vats are not comparable to the vat of pastel and the vat of indigo, by means of which much more work is dispatched; they can only answer in small dyehouses.

For dyeing silk blue, the indigo vat above described is employed. More indigo is usually put in than the dose which has been indicated; but the proportions of bran and madder are nearly the same. Macquer states,\* that if a weight of madder equal to one-fourth of the *cendres gravelées* be introduced, the vat becomes green, and its colour is surer on silk, without having a less agreeable cast. The pastel vat and the others spoken of are not fit for dyeing silk, because they do not colour with sufficient promptitude.

When the vat is in working condition, there is given it what is called a *brevet*, with about two pounds of *cendres gravelées*, and four ounces of madder. It is raked up; and after four hours it may serve for dyeing. The heat should be then sufficiently reduced, so that the hand may be held in it without pain.

The silk, previously boiled with soap in the proportion of 30 per cent. of its weight, and then well cleared of its soap by two beetlings, or even more, in running water, is plunged into the vat. As it is very liable to take the colour unevenly, it must be dyed in small portions. The workman, therefore, immerses the hanks, one after another, passing them round a cylinder of wood; and when he has turned them several times in the bath, he wrings them forcibly over the bath, and airs them to make the green become blue. When they appear perfectly ungreened, he throws them into pure water, and then wrings them several times with the *espart*, (pin.)

We must take care that the silk just dyed should be very speedily dried. During winter and damp weather, it is dried in a chamber heated by a stove, exposing it on a kind of frame which is kept in constant agitation.

When the bath grows weak, and its green colour diminishes, a *brevet* is given it, into which there enter one pound of *cendres gravelées*, a little madder, and a handful of well washed bran. When the indigo is found to be exhausted, more of it must also be restored to the bath, along with the due proportions of *cendre gravelée*, madder, and bran.

\* Art de la teinture en soie.

Some dyers turn to advantage the weakened vats for dyeing light shades ; but the blue obtained in this case is less beautiful and less permanent, than if for these shades fresh vats were used, into which a smaller quantity of indigo entered.

Indigo alone cannot give a deep blue to silk. For this purpose it is necessary to prepare it, by giving it another colour or ground. For turkey-blue, which is the deepest, a very strong bath of archil is first given, and one a little weaker for king's blue. It is then turned through a fresh and well furnished vat. The other blues are made without any ground.

A blue as deep as king's blue is also made, for the ground of which cochineal is used instead of archil, with the view of giving it more solidity, which occasions it to be called *fine blue*.

By means of verdigris and logwood, a blue which possesses very little solidity is given to silk. But its durability may be much increased, by giving it first of all, by this means, a lighter shade than what is wished for, next passing it through the archil bath, and finally through the vat.

To dye raw silks blue, such must be chosen as are naturally white ; they must be well soaked in water, and then turned through the vats in separate hanks, like the scoured silks. Raw silks take the dye generally with more facility and activity than those which have been boiled. The boiled should, if possible, be passed through the vat before the raw. If raw silk require archil, or the other ingredients above mentioned, it is to be treated like the boiled silks.

According to Le Pileur d'Apligny, the vat for dyeing linen and cotton is a cask capable of holding nearly 109 gallons. The quantity of indigo employed is usually from  $6\frac{1}{2}$  to  $8\frac{1}{2}$  pounds. This indigo, after being ground, is boiled in a ley, run off clear from double its weight of potash, and lime equal to the weight of the indigo. The boiling is continued till the indigo is well penetrated with the ley, stirring the mixture with care, and taking pains to prevent the indigo from sticking to the bottom, and burning.

During the boiling of the indigo, an equal weight of quick-lime is to be slaked ; to this about four gallons of hot water are added, and sulphate of iron is dissolved in it to the amount of double the lime. When the solution is finished, the liquor is poured into the vat, which should be previously half filled, or

nearly so, with water. There is afterwards poured over it the solution of the indigo, and the remainder of the ley which had not been employed in the boiling is added. When the whole has been poured into the vat, it must be filled up with water, to within two or three finger-breadths of the edge. It is stirred with the rake two or three times a-day, till it be in a condition for dyeing, which takes place at the end of 48 hours, often sooner, according to the warmth of the air, which accelerates, more or less, the formation of this vat.

Some persons add to a vat, composed nearly like the preceding, a little bran, madder, and pastel.\*

At Rouen another process is followed, which Quatremere has described. The vats are constructed of a species of gun flint; the inside and outside are covered with a kind of coating, made with a fine cement. A certain number of these are placed in one dyehouse, arranged in one or several parallel lines.

A vat may contain four hogsheads of water, and there may be put into it from 20 to 22 pounds of indigo, previously macerated, during eight days, in a caustic ley, strong enough to float an egg. This indigo is then ground in a mill, in which, indeed, the maceration frequently takes place. The vat is then filled, with the exception of a small space, and 22 pounds of lime are introduced into it. When it is well slaked, the vat is raked, and 40 pounds of sulphate of iron are put in. Whenever the solution is completed, the mill-ground indigo is poured in through a sieve. The vat is raked seven or eight times the same day; and, after a repose of 36 hours, it may be used for dyeing.

There must be vats established at different periods. They begin by passing the cotton or yarn through the most exhausted vat, and they continue thereafter to proceed from vat to vat till they come to the strongest, unless before reaching it the wished-for hue is obtained. The cotton or yarn must be wetted before entering the first vat. It should not be left more than five or six minutes in the bath, because it takes up in this time nearly the whole blue with which it can charge itself.

When the dyeing in one vat is over, it must be raked up, and no longer worked upon, till it settle at least 24 hours. If it is recently set, however, it does not need to stand so long.

\* Procès-verbal des opérations de teint faites à Yvetot par François Gonin.



When a vat has been dyed with three or four times, it begins to be altered. When raked, no more blue veins are perceived at its surface, where it becomes black. In this case, it must be replenished, for which purpose,  $4\frac{1}{2}$  pounds of sulphate of iron, and two of quicklime, are added, and it is twice raked. The vat may be replenished three or four times, diminishing its ingredients in proportion as it declines in strength and quality.

In the vats just mentioned, it is the potash and lime which give solubility to the indigo deoxydized by the action of the precipitated iron. It may be thence inferred, that the sulphate of iron employed should be little oxydized, for in a state of high oxydation it produces no effect.

Lime may be used alone for precipitating the sulphate of iron, and dissolving the indigo. In this case, the solution of indigo is less concentrated, and we cannot succeed, or at least we cannot succeed so quickly, in giving to cotton or thread so intense a blue by means of that vat, as by the preceding. But this circumstance is even frequently of advantage. Some persons increase the concentration of this vat, by adding to it a little orpiment and potash.

Bergmann and Haussman have given particular descriptions of this vat, with proportions a little different. The latter remarks on this occasion, that the sulphate of iron must not contain copper, for the oxyde of copper restores the indigo, which it is our interest to keep in a state of deoxydation till it be combined with the stuff. This observation is applicable to all the cases in which sulphate of iron is used along with indigo. He further remarks, that cotton cloth passed through water acidulated with sulphuric acid, on its quitting this vat, assumes a finer blue than if it be merely washed in the river, or set to dry.

We shall now point out a vat of this kind, the good constitution of which is confirmed by experience; as also the different uses that may be made of it.

The proportions employed for this vat are one part of indigo, two of sulphate of iron, and two of lime. After raking it for several hours in succession, when we set it, it is allowed to settle two days; we then dye with it.

Before dyeing, the froth is removed; and every evening,

after the day's work is over, the replenishment is given to the vat, by putting into it some liquor (*bouillon*) from a little vat prepared for this purpose, with a much smaller proportion of water than there is in the dyeing vat, to which the froth of the latter is added. It is raked, covered up, and left at rest till the work be resumed. When the vat is weakened, a little power is communicated to it by the addition of some lime, and sulphate of iron.

For the dyeing of cloths, they must be stretched upon frames, fixing their selvages to little hooks (pins) with which the cross-bars of the frames are provided. By means of a rope, running over a pulley, the frame is dipped into the vat. A slight agitation is given to it for a little while, to moisten the cloth more equably; the frame being so suspended that the whole breadth of the piece may be in the vat, without allowing the bottom of the frame to touch the sediment. After letting it become blue, (in the air,) it is washed with care, especially if *preserves* (resist pastes) be printed upon it. In order to dye two blues along with white, (spots,) the reserve is impressed, which should cover the white and the pale blue. It is dyed, washed, and the reserve is a second time applied to the places which are to remain white: such as have been reserved at the first dyeing, not being so at the second, take a lighter hue than the ground of the cloth. When the reserved places are to be dyed after the blue dye, the mordant is mixed with the reserve.

The property which the oxyde of copper possesses of giving up its oxygen to indigo, and thereby depriving it of its power of fixing on stuffs, is made use of for reserves.

The reserves are usually composed of verdigris, pipe-clay, and several substances, which vary in different receipts. The verdigris is the only active one: the pipe-clay kept in suspension by the mucilage, which serves to thicken the reserves, may have the advantage of lessening the quantity of mucilage necessary for the thickening, and rendering the reserve more easy of application. To the verdigris, sulphate of copper is usually joined, and sulphuric acid is added, undoubtedly with the view of rendering this salt more soluble. The composition of a good reserve resolves itself into the employment of the most soluble solution of copper; 1. For applying more oxyde to the stuff; and 2. That its crystallization may not make it difficult to print

on. For very deep blues, however, which require a long continuance of the cloths in the vat, some substance must be added to the reserve that may prevent it from dissolving in the vats. With this view, tallow or wax is intermixed, while the reserve is heating so as to thicken it. The compositions formerly used for reserves, owed much of their effect to the wax. It was kept in solution, (fusion?) in order to be applied on the cloth, where it formed a kind of varnish that was removed by hot water after the dyeing.

If it be wished to give cloth blue figures on a white ground, a style of work called *China blue*, or *English blue*, this process is divided into different stages. The ground indigo, mixed with sulphate of iron, is printed on the cloth, which is stretched on a frame similar to that above described, and passed through a vat containing lime. Here it remains for some time. It is then plunged into a vat which contains a solution of sulphate of iron, marking from  $3\frac{1}{2}^{\circ}$  to  $4^{\circ}$  of the areometer of Baumé, 1.025 sp. gravity. It is now returned into the quicklime vat, passing thus alternately four times from one of these vats to the other. When it quits for the fourth time the vat of sulphate of iron, it is plunged into a vat containing a feeble alkaline solution, in which it remains an hour, and lastly, into a fourth vat holding sulphuric acid diluted with water.

What occurs in a vat, takes place here on those parts of the cloth to which the indigo and sulphate of iron has been applied. The sulphuric acid dissolves away the oxyde of iron with which the cloth is covered. To remove it completely, the cloth must be turned through this acid kept hot in a leaden boiler.

To have patterns in china blue, bearing different shades, it is sufficient to put into the colour printed on, different quantities of indigo.

Bergmann describes another vat, very convenient and expeditious, for thread (yarn) and cotton, which is described also by Scheffer.\* A very strong solution of alkali is taken; 186 grains of well-ground indigo are added to it for every  $1\frac{1}{4}$  pints of liquid. After some minutes, when the indigo is thoroughly penetrated with it, 372 grains of powdered orpiment are put into the liquor, the bath must be well raked, when, in a few

\* *Essai sur l'art de la teinture.*

minutes, it becomes green, forms a blue froth, and shows a pellicle. The fire should now be extinguished, and the dyeing may be commenced.

This vat does not differ from the preparation applied to cotton cloths, which is called pencil-blue, except in the proportions of orpiment, and especially of indigo, which are much larger than in the latter. For this preparation there is employed, according to Haussman, for 220 pounds of water, 33 of potash, 13 of quicklime, as much orpiment, and  $17\frac{1}{4}$  of indigo. Oberkampf, the whole of whose processes have been improved with so much care, employs a still greater portion of indigo. In the process of Bergmann, the indigo constitutes nearly the 24th part of the water; still less in that of Scheffer; 1-12th in that of Haussman, and 1-9th in that of Oberkampf. The proportions of the other ingredients vary in these different processes. It would seem, that these preparations may succeed within a scale very extensive as to the proportions; nor would it be easy to determine what are the most advantageous ones for the object proposed.

Three processes are employed for giving blue in the art of calico-printing.

The first of these processes is used for dyeing cloth whose ground is to be blue or green; and whenever they bear colours which are to be kept from varying in the vat, these are covered with the white reserve.

If the cloth is to retain a white ground, and bear blue figures, of one shade or of several, the second of these processes is had recourse to. Sometimes one or two colours are joined to the blue thus made; but in this case, they must be applied after the blue dyeing, because there is not a colour which may not be either destroyed, or powerfully altered, in the operations which it requires.

Lastly, in other circumstances, a blue is to be put on cloth covered with a pattern, all of whose parts are already coloured, and which leaves merely small spaces to colour blue. For this purpose, the blue is used which is applied with the pencil.

This blue of application is thickened with gum, and put upon the pencil. It may be printed on, by covering with canvass the frame which contains the thickened colour, and removing the regenerated indigo with a scraper before applying the plate; but

only small objects of a slightly intense blue, which rarely succeeds, can be thus applied.

Bancroft says, that he has substituted sugar for the sulphuret of arsenic with success; which would be advantageous, on account of the price and poisonous qualities of this substance. The experiment did not succeed with us.

The blue of application has been attempted to be prepared by means of the oxyde of tin; but the degree of concentration of the alkaline solution adequate to the solution of the oxyde and the indigo has not been hitherto ascertained, so as to be susceptible of thickening with the gums. This point once determined, a pencil blue will be had, which will possess the very great advantage of not occasioning a bulky deposite, which always embarrasses the vessels where this blue is made in the ordinary processes, and which, however well washed, causes a considerable waste of the indigo.

In printing on cloth, ground indigo with oxyde of tin, and passing the cloth through a solution of oxyde of tin in potash, china blues may be made in a single vat. We have been able to make in this way only light blues. Were this process brought to the point of producing more substantial blues, it would afford great advantages.

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## CHAPTER IV.

### *Of Saxon Blue.*

THE name of *Saxon blue* is given to the dye for which solution of indigo in sulphuric acid is employed, because it was discovered at Grossenhayn, in Saxony, by Counsellor Barthe, about the year 1740. This discovery was kept secret for some time, but it gradually spread abroad. At first the solution was not made with indigo alone, but alumina and antimony were added, and other mineral substances besides, which were previously digested with the sulphuric acid. Indigo was afterwards added, and when the solution was complete, it was used for dyeing.

Bergmann performed many experiments on this solution of

indigo, which have thrown a great light, not only on its properties, but also on the general cause of the fixation of the colouring particles on stuffs.

He employs, as has been stated before, one part of indigo well pulverized with eight parts of sulphuric or vitriolic acid, so concentrated that its specific gravity is to that of distilled water as 1.90 to 1.00. The mixture being made in a glass bottle, loosely stopped, a great heat is excited. After a digestion of 24 hours, at a temperature of 77° or 100° Fahr., the indigo is dissolved, but the mixture is entirely black and opaque. On adding water it grows clear, and yields successively every shade of blue, according to the quantity of water. In a great number of experiments which this illustrious chemist describes, he kept in boiling water for 24 hours the stuff intended to be dyed: he then put a determinate weight of it into a bath of greater or less strength, till the bath was deprived of colour. It follows from his experiments, 1. That one part of indigo by this process can produce a black blue on 260 parts of stuff, which seems to be then saturated, for it could take no more indigo in a permanent manner. 2. That the cold bath acts as well as the hot. 3. That the operation may be made without waste of indigo, for the bath can be entirely blanched, and if it has been too much charged, unsaturated stuff may be added, which absorbs all the remaining colour. 4. That the bath saturated with salt of soda (crystallized carbonate) yields only a very pale colour: and with the sulphate of soda it gives a bright blue, but much less feeble, so that these salts unite more or less with this dye.

Similar experiments have been made on silk, which had, in like manner, been soaked in hot water, and which had been withdrawn from the bath after 144 hours. The indigo dye forms a blue on silk as on (woollen) stuff; but the affinity which precipitates the blue molecules is weaker. Although the patterns of silk resist water alone very well, they cannot bear the action of soap.

Threads and cotton took but very pale shades with this dye.

The deepest shades obtained by this process with the employment of concentrated sulphuric acid are not liable to change, according to the statement of Bergmann. He says, that having exposed to the sun all the patterns during two months, the Persian and Turkey blues (Coventry blues) were scarcely impaired;

but that the light shades suffered much more, growing dead and greenish.

Quatremere says, that among several dye-houses, he was acquainted with only two where the method of making the indigo dye, by sulphuric acid, penetrate into the interior of the stuff, or what is called pierce or cut, (*percer ou trancher*,) was understood; and that he gave it this property by introducing fixed alkali into it, in the proportion of one part to one of indigo, with six of sulphuric acid. He has dyed with this preparation a sample of blue of the liveliest and deepest shade, and the section was as dark as the surface.

Poerner, who was much occupied with this preparation, recommends likewise the addition of alkali.\* He says, that by this means the colours are more agreeable, and penetrate deeper. He further prescribes to take only four parts of sulphuric acid to one of indigo. In the process which he describes, four parts of concentrated sulphuric acid are poured on one part of indigo reduced to a fine powder. This mixture is stirred for some time, and then left at rest for twenty-four hours. One part of good dry potash in fine powder is now added to it. The whole is well mixed, and left at rest for twenty-four hours, after which a greater or less quantity of water is added to it.

The same author announces, that he has found a preparation of indigo in a dry form, which is more advantageous, and of more easy and convenient use than the preceding, but that he cannot communicate it yet to the public.

Bancroft adopts the proportion of sulphuric acid and indigo, as also the addition of alkali, recommended by Poerner. He says, that the sulphuric acid may be even diluted to a certain degree. He remarks, that the indigo of Guatemala is fitter for this solution than the others, ascribing this peculiarity to its being more oxydized, because lime water was probably not employed in its preparation; on which account it was necessary to subject it to longer beating to effect its precipitation. The difference presented in this respect by Guatemala might, however, be owing only to its affording less yellow extractive matter, and to its molecules offering in their cohesion less resistance to the sulphuric acid.

\* Instruction sur l'art de la teinture.

Bancroft states, that by precipitating the solution of indigo with carbonate of lime a blue precipitate may be had, which can serve for dyeing directly. This might possibly be the preparation announced by Poerner.

Bergmann conceived, that the Saxon blue owed its little permanence merely to the too feeble concentration of the acid which he employed for dissolving it. But his trials must have led him into a mistake in this respect.

For regulating the preparation and employment of solution of indigo, what we have formerly laid down must be borne in mind.

The indigo suffers in this solution an alteration which cannot be avoided; but it should be so managed as to make it as small as possible. Consequently the heat should be tempered as nicely as may be, as well as the concentration and quantity of the sulphuric acid. When the solution is made, it is proper to dilute it with water, in order to preserve it, and to prevent the degradation making progress.

A small quantity of alkali may have good effects, but a greater would be injurious, since the alkali possesses the property of dissolving the blue molecules precipitated from the sulphuric acid. Thus, as Haussman observes, soap and alkalies render stuffs dyed in Saxon blue yellow, and water alone is sufficient to separate the colouring particles fixed on cotton.

In the process commonly made use of for dyeing Saxon blue, the cloth is prepared with alum and tartar. A smaller or greater proportion of the indigo solution is put into the bath, according to the lightness or depth of the shade wished to be obtained. The name *composition* is given in the workshops to this solution, and occasionally that of *bleu de Prusse*, or Saxon blue. The clear shades may be made in the sequel of the deep shades, but they have more lustre when made in a fresh bath. For the deep shades, it is advantageous to pour in the solution of indigo by portions, lifting up the cloth on the reel.

Other details will be given on this dye, and particularly on the *English blue*, which is a modification of it, when treating of green in the Sixth Section.



## CHAPTER V.

*Of Dyeing Blue by means of the Prussiate of Iron.*

As the prussiate of iron, or prussian blue, furnishes a beautiful and permanent colour to painting, attempts have been made to extend its use to dyeing. It was Macquer who sought to render this substance useful to the art, after giving important observations on its nature.

The chemical properties of the principle which forms prussian blue with the oxyde of iron, occasion very varied combinations and phenomena, of which we shall give merely such an idea as may be proper for regulating the operations in which it is employed.

This principle is derived from a combination which is formed when any charcoal containing azote, as that of animal substances, is calcined along with alkali, and then moistened. The water is decomposed; its hydrogen, on the one hand, forms ammonia with the azote, and, on the other, forms the colouring principle of prussian blue with azote and carbon, whilst its oxygen produces carbonic acid. If the charcoal has been exposed to too strong a heat, it is deprived of its azote, as Gay Lussac observed, and then it can no more produce either ammonia, or the colouring principle of prussian blue.

The name of *acid* is given to this colouring principle. It has not, however, of itself this property, but acquires it by combining with a metallic oxyde, particularly the oxyde of iron; for it then saturates the alkaline properties. As it is in this state that it exists in the alkaline prussiates, we shall call it by this name, without regard to its complex composition.

Whenever an alkali is made to act on the prussiate of iron, the prussic acid, which retains some oxyde of iron, saturates the alkali, and thus the prussiates of alkali are obtained. The oxyde of iron meanwhile retains a certain proportion of prussic acid. This latter compound has a yellow colour. In this state an acid makes a partition of the oxyde of iron, till the yellow prussiate be brought to the state of blue prussiate. At this term the acids can no farther destroy the combination, unless heat be employed.

The acids cannot all equally decompose the prussiates of

alkali without an elevation of temperature, or without the agency of light. In this case a portion of the prussic acid assumes the elastic state, and volatilizes, whilst another falls down with the oxyde in blue prussiate.

If a solution of iron be mixed with a prussiate of alkali, the oxyde combines with the prussic acid, and precipitates; but it retains a portion of the alkali in its composition, so that the prussiate of alkali and prussiate of iron must be considered, both the one and the other, as triple combinations. In the one it is the oxyde which predominates; in the other it is the alkali. Let us examine the methods by which we can fix this first combination upon stuffs.

Macquer's first attempt was to soak cotton yarn, wool, and silk, in a solution of alum and sulphate of iron; next in an alkaline solution, which was in part saturated with prussic acid; then in water soured with sulphuric acid, so as to dissolve the portion of the oxyde of iron combined with the prussic acid, which had been precipitated by the alkali uncombined with this acid. He repeated the immersions successively, and obtained a fine blue, but very unequable. Wool and silk became rough to the touch, by the action of the alkali, as well as by that of the sulphuric acid.

It is easy to see that this process ought not to have been successful; for as an alkali not saturated with prussic acid was used in a second immersion, the portion of unsaturated alkali must have dissolved more or less of the blue fixed in the first. If these experiments were therefore to be resumed, it would be requisite to employ an alkali saturated with prussic acid or lime water, and particularly magnesia, which have likewise the property of combining with this acid.

In a second process this able chemist boiled his patterns in a solution of alum and tartar, and turned them afterwards through a bath, in which he had mechanically diffused prussian blue. They were now died evenly, and were soft to the touch, but the shade was faint; nor was it possible to make it deeper.

Menon proposed another process for thread and cotton. It consists in dyeing the stuff at first black, and then letting it steep some minutes in a solution of prussiate of alkali. It is thereafter boiled in a solution of alum, where it takes a very deep blue. A blue combination is formed, and the alum dis-

solves the remaining black particles; but the effect must be very irregular, according to circumstances.

Several attempts have been made to derive advantage from these experiments, and especially from the first method; but whatever pains may have been taken, the colour was always faint, dull, and unevenly. This was given up in favour of a process which has a considerable relation to the second one of Macquer. The prussian blue is merely diffused in muriatic acid, which does not make a true solution, but attenuates it enough, by its affinity, to cause it to penetrate cotton goods more copiously. We shall now literally transcribe the description given of it by Roland de la Platiere,\* which agrees with the practice of certain dyers.

On fine prussian blue powdered, passed through a very close sieve, and put into an earthenware vessel, in an indeterminate quantity, but in the proportion of half a kilogramme (about a pound) for every piece of goods, pour muriatic acid till the materials assume the consistence of syrup; stir continually while it is in fermentation (chemical action) for about half an hour; dilute well, and stir again from hour to hour, during a day, till finally no more fermentation is perceived. Thus the division of the particles will be very great, and their union with the acid intimate.

Into a trough narrower than the ordinary ones, and more widened out above, two feet and a half high, two feet in diameter at the bottom, and two feet and a half at the top, put from seven to eight gallons of water for one piece of velvet; add to it some of the composition, previously well diluted with water in a separate vessel. Pour this into the bath through a very fine sieve; and as soon as the piece is arranged on the winch placed over the trough, rake the bath well, and let down the velvet quickly, working with the utmost possible activity, for one, two, or three hours, passing the piece in succession from the winch to the horse or board, (*planche*,) and from the board to the winch.

As the prussian blue is not really dissolved, but only much attenuated, and as it is heavy, it falls down rapidly on the stuff, (*matière*,) and always in larger quantity on the first that presents itself. It thus happens, that the colour is at first wavy, and

\* L'Art du fabriquant de velours de coton.

often in patches, (*placardée*,) whatever pains be bestowed. This should excite no surprise. Such accidents must, however, be avoided as much as possible, by working the stuff over and over again, washing with the bath itself the portions most stained, working over again, sometimes one end first, sometimes the other, and then drying; lastly, working anew, always as equally and quickly as possible. It may now be dried a second time, if necessary, and worked once more till the wished-for shade appear, and the colour be very even. This dye requires the most expert of workmen. Between each drying the stuff is washed and beetled. In all kinds of baths the stuffs must always be previously moistened. Were it dry, the bath would penetrate with difficulty and great inequality. The last time they do not wash, but dry on the pole, in the open air, either in sunshine or shade, provided the piece be well stretched.

This colour, one of the most beautiful that art can produce, is unalterable in the air, and in all weathers, when it is well done. Roland de la Platiere exposed several patterns of it for six months consecutively; the colour heightened (*raomenté*) for some time, and finally lost somewhat. The acids are not injurious to it; even boiling in alum affects it slightly; dust, however, and friction on the creases of it, soon makes it fade.

The methods heretofore pointed out for fixing the beautiful colour of prussian blue on stuffs, have not accomplished this object. The first, which form a combination, yield only a weak or very unequal colour; the last afford but a mechanical fixation of blue molecules, which a slight friction can separate. It has been attempted to give more effect to the method of combination.\*

A combination can be produced between the prussiate of iron and a stuff, only when the oxyde of iron is previously combined with the stuff, so as to receive the prussic acid, because it (the compound) is insoluble, resembling indigo in this respect; but on impregnating a stuff directly with a solution of iron, in order to combine it with the oxyde of this metal, inequalities are inevitable, which become very obvious when they are changed into prussiate. This inconvenience is obviated in dyeing the stuff first grey or a deeper shade, according to the blue wished to be

\* *Annales de chimie*, tom. xxi.

obtained; for in this primary dye, a more uniform combination is made of oxyde of iron and of astringent matter with the stuff.

An alkaline prussiate would not give up the prussic acid to the stuff; but on adding an acid, as the sulphuric, the action which this exerts on the base of the alkaline prussiate determines the separation of the prussic acid, which now enters into combination with the oxyde of iron united to the stuff, expels the astringent from it, and takes its place, forming a fine blue colour. All the alkaline prussiates may be employed with this view.

The process which has been pursued, consists in diffusing, in three or four parts of water, the prussiate of lime, or in dissolving a corresponding quantity of the prussiate of alkali in the water; in keeping the liquor at a heat of 77° to 100° Fahr. and plunging into it for some time the stuff previously dyed, of a shade more or less deep, from grey to black. It is proper to begin with soaking it in hot water, and on taking it out of the liquor, to turn it through cold water. Sulphuric acid answered better than the muriatic. This method may be especially useful for procuring fine greens. We shall treat of it elsewhere.

The trials were only made on cotton and silk. Bancroft has found the process equally successful with wool.

The property possessed by the prussiates, of forming blue by giving up the prussic acid to the oxyde of iron, may render them useful on employing them in the same manner to restore the colour of black stuffs, whose astringent has been destroyed by age, and in which the oxyde of iron, grown predominant, produces a russet hue. They may also deepen the imperfect blacks. Thus a mixture of blue and black is made, which increases, as we have seen, the intensity of the latter.

The products of the prussic acid process, which we have just now detailed, have the great inconvenience of being destroyed by the action of alkalies and soap, because the alkalies decompose the prussiate which is formed. This is a serious disadvantage, particularly for cotton stuffs. If it be used, therefore, on such stuffs, bran or other detergents should be employed, instead of soap, for cleansing them.

Bancroft has made several interesting experiments, with the view of applying the other metallic prussiates to stuffs. He

obtained, in particular, a fine copper-red colour, by using solutions of copper. We have got this colour by impregnating cotton with a solution of copper, and following, in other respects, the process just described. Hatchet also made use of solutions of copper for forming, by means of the alkaline prussiates, a prussiate of copper, of a red bordering on brown, which presented interesting properties when employed as a colour, (pigment.)\*

The celadon green was formerly given by means of sulphate of copper; but this colour, which approaches very near to blue, is not permanent, and is no longer in use. The processes employed in it may, however, be pointed out. The cloth, washed in the fulling-mill, and moistened with hot water, is turned through a well saturated solution of soap, for about an hour, when it is passed for half or three quarters of an hour through a solution of sulphate of copper or blue vitriol: by means of a net, the cloth is prevented from being made dull with the sediment of the soap and the sulphate of copper. Occasionally, for obtaining a more decided green, a solution of copper was mixed with the weld bath; sometimes verdigris was substituted for sulphate of copper.

Hellot describes a somewhat different process, by which the Dutch produced this colour in perfection. He says that they mixed equal parts of lime and sulphate of copper in a bag; and that they turned the cloth out of the boiler which contained the solution of soap into another adjoining one, where the particles of copper which escaped through the bag made it green.

The blue colours procured by means of logwood, of which we shall speak more particularly when treating of the properties of this colouring substance, cannot be compared, in point of durability, to those given by indigo and prussiate of iron.

\* *Bibliot. Britann.* vol. xxii.

In the trials of the metallic prussiates, it must not be forgotten that the alkaline prussiates contain prussiate of iron, which falls down in the operation; whose colour may make that of the other prussiate to vary. If this be soluble, a result may be ascribed to it, which is in reality owing merely to the prussiate of iron.

## SECTION III.

### OF RED.

#### CHAPTER I.

##### *Of Madder.*

MADDER, a substance very extensively used in dyeing, is the root of a plant, of which two species are distinguished by Linnaeus. The first, the *rubia tinctorum foliis senis*; the second, *rubia peregrina foliis quaternis*. The first has two varieties, the cultivated and the wild madder, also named *rubia silvestris monspessulana major*.

Although madder can grow both in a stiff clayey soil and in sand, it succeeds better in a rich, soft, moist, and very slightly sandy soil. It is cultivated in several of our departments. That of Zealand was generally regarded as the best which grew in Europe; but the madder cultivated in the lower departments of the Rhine is not inferior.

Madder, prepared for the purpose of dyeing, is distinguished into different qualities. That which comes from the parent roots (*mères racines*) is called *garance grape*; and *non grape* is the produce of the stems that sink into the earth, where they are transformed into roots, to which the name *couchis* (layers) is given. Each of these species is subdivided into *garance-robée*, *mi-robée*, *non-robée*, short or male, (*courte ou mâle*.)

When the roots of the madder are plucked up, the *couchis* are separated to form the madder *non grape*, to which are joined the fibres that have not attained a certain size, as well as the roots which are too large, and contain much heart or ligneous substance. The best roots are those which have the size of a writing quill, or at most of one's little finger. They are semi-transparent and reddish, have a strong odour, and a smooth bark.

The madder, taken from the ground and picked, should be dried in order to be ground and preserved. It is dried in warm climates in the open air; but elsewhere stoves must be employed.

It results from this difference of preparation, or perhaps also from a variety in the plant, that two kinds of madder are distinguished, which differ in their dyeing properties.

The first, which is cultivated at Smyrna, in the island of Cyprus, and in the Levant, is known under the name of *lizari*. Its culture is established in our southern departments, where it is by no means of worse quality. We shall now take a summary view of the preparation to which it is subjected in our departments of the south, agreeably to notes given us by Chaptal. We shall afterwards speak of the ordinary madder.

The roots are dried in the air, on a paved floor, or on a hurdle. They are stirred about with a fork, and slightly beat, in order to separate the epidermis (outer skin) and the earth. What remains on the ground, composed of earth, epidermis, and small roots, is sifted, and that left on the sieve forms what is called *billou*, common madder, which is fit for only dull colours. The roots of madder thus picked, are ground, either under a stone mill, or under knives similar to those of a bark mill (tan mill.) By means of fanners or a boulder, there is separated, after a first milling, the madder called *non-robée*. It is composed of a residuum of earth, epidermis, and bark. After a second milling, what is separated is called *mi-robée*. Finally, after a third milling, the madder *robée* is obtained, which is of the best quality. The *mi-robée* is preferable, however, when it comes from somewhat thick roots. When milling is performed for one's own use, only one quality is made; or if a very brilliant colour be wanted, the worst quality is separated by a first grinding, and the product of the second is employed. This is called in the south, *grappier*.

The roots of good quality are of middling size, little branchy, (*peu rameuses*), and their fracture is of a lively reddish yellow. Such as grow wrinkled in the course of drying are not good. For the madder to be properly ripened, it should have reached its third year, and be plucked in the fourth.

The preparation of madders is carried on in the departments of the Rhine by more numerous operations.

The roots are dried in a stove, heated by means of a furnace, from which the air is allowed to issue only at intervals, at the



moment when it is judged to be saturated with moisture. The furnace (flue) occupies a great portion of the floor; above, are three open floors, on which the roots are distributed in layers of about two decimeters (nearly 8 inches.) At the end of 24 hours, those which are on the first stage (or floor) directly above the stove are dry, when they are taken away and replaced by those of the superior floors. This operation is repeated whenever the roots over the stove are dry. The dry roots are thrashed with a flail, passed through a *talard* similar to that employed for corn, and then passed through a very coarse sieve. What passes through is farther thrashed, *talardé*, and sifted through a finer sieve than the first. These operations are repeated five times, proceeding successively to sieves still finer and finer, and setting aside every time what remains on the sieve. What passes through the fifth sieve is rejected as sand and dust. After these operations, the whole roots remaining on the sieve are cleaned with common fanners, and women separate all the foreign matters which had not been removed before. For dividing the roots, thereafter, in different qualities, a brass sieve is made use of, whose meshes are from six to three millimetres in diameter, (from 1-4th to 1-8 inch. E.) What passes through the finest is rejected; and what passes through the coarsest is regarded as of the best quality. These roots, thus separated, are carried into a stove, of a construction somewhat different from the first. They are spread out in layers of about a decimeter in thickness, (nearly 4 inches E.) on large lattice-work frames, and the drying is known to be complete, when on taking up a handful and squeezing it, the roots break easily. On quitting the stove, the madder is carried, still hot, into a machine, where it is rasped, and a sieve separates the portion of the bark reduced to powder. This operation is repeated three or four times, then the boulder is had recourse to. What passes through the sieve, or the brass meshes of the boulder, is regarded as common madder, and what issues at the extremity of the boulder is called the flour. Lastly, the madder which passes through the boulder is ground in a mill with vertical stones, and then passed through sieves of different sizes. What remains above is always better than what goes through.

The madder of Alsace is reduced to an extremely fine powder, and its colouring matter is extracted by a much longer

ebullition than is necessary for the *lizari*. The prepared madders ought to be carefully preserved from humidity, because they easily imbibe moisture, in which case fermentation spoils their colour.

D'Ambourney and Beckman have asserted, that it is more advantageous to employ the fresh root of madder than what has been submitted to desiccation, especially by means of stoves. But in its state of freshness, its volume becomes troublesome in the dyeing bath, and uniform observation seems to prove that it ameliorates by age. Besides, it must be rendered susceptible of keeping and carrying easily.

The celebrated Watt made experiments on a very choice madder from Zealand, which are well adapted to display the properties of its colouring particles. We shall detail them.

A. This madder is of a brownish orange colour, and of the consistence of a coarse powder, possessing a slight degree of cohesion: it attracts moisture, in which case it loses its properties, so as to become unfit for the purposes of dyeing.

B. With water it affords an infusion of a brownish orange colour; its colour cannot be extracted without a copious addition of water. Margraff directs three quarts of water for two ounces of madder. Its colouring particles may be extracted either by hot or cold water; to the latter it appears to give a more beautiful colour; its decoction is brownish.

C. When an infusion or decoction of this drug is slowly evaporated in an open vessel, a pellicle is formed on the surface, which gradually falls to the bottom; after which fresh pellicles are successively formed until the evaporation is finished.

D. The extract thus prepared is of a dark brown; it partly dissolves in water, to which it communicates a lightish brown colour.

E. The infusion set to digest for some days in an open vessel, which should be of such a height that the liquor reduced to the form of vapour may fall back again, deposits dark brown pellicles. The liquor remains of a brownish colour, and the pellicles are soluble in water, but with difficulty.

F. Alum forms in the infusion B a deep brownish red precipitate, composed of pellicles, and the supernatant liquor is of a yellow colour, inclining to brown.

G. Fixed alkalies precipitate from this last liquor a lake of a

blood-red colour, which has greater or less intensity, according to the quantity of alum that has been dissolved in it. In this way, a blood-red lake may be obtained; but we cannot, by any means hitherto known, give it the brightness of cochineal lake; in oil it is transparent, but in water it is opaque, and without beauty.

H. If a superabundant quantity of alkali be employed, the precipitate is re-dissolved, and the liquor becomes red.

I. The lake precipitated by potash is of a more beautiful colour than that by soda.

K. Calcareous earth precipitates a more dark and brown coloured lake than alkalies, particularly if it form lime-water.

L. If a few drops of alkali be added to the water employed in making the infusion B, the infusion extracts many colouring particles of a deep red bordering on brown. 1. Alum precipitates a deep brown lake from this infusion. 2. Acids added in small quantity change it to a yellowish colour, and in greater quantity render it a brown yellow; but they precipitate nothing from it. 3. This infusion, evaporated to dryness, forms a gummy extract, which easily dissolves in water.

M. If the infusion B be made with water very slightly acidulated with a mineral acid, it is yellowish. 1. This liquor, by long digestion, becomes of a greenish-brown, and the yellow appears to be destroyed. 2. The addition of an alkali restores the red colour; and the infusion then affords, on evaporation, an extract, which readily dissolves in water.

N. If carbonate of magnesia be added to the water used for the infusion B, the infusion is of a clear blood-red, and on evaporation forms a blood-red extract, which readily dissolves in water. 1. A solution of this extract, which is employed as a red ink, when exposed to the light of the sun, becomes yellow. 2. Alum precipitates from this infusion a small quantity of an ill-coloured lake. 3. Alkalies give it a redder and more fixed colour.

O. If the infusion be made with a solution of alum, it is of an orange yellow. This infusion, precipitated by an alkali, affords a lake resembling that of F, but its colour is not so good.

P. A solution of sugar of lead, added to the infusion B, forms a brownish-red precipitate. 1. A solution of mercury in the nitric acid, gives a purple-brown precipitate. 2. A solution of

sulphate of iron, a fine bright brown precipitate. 3. A solution of sulphate of zinc has not been tried. 4. A solution of sulphate of manganese, a purple brown precipitate. 5. A solution of iron in aqua regia has not been tried.

Q. The infusion B being mixed, while hot, with the infusion of cochineal, a brownish-red precipitate, bordering on a deep purple, was formed, of difficult solubility in water. By continuing the digestion, a greater quantity of this precipitate appeared. 1. A pattern soaked in the preparation which the linen printers use, having been dyed in this mixture, took a brownish-red colour; and after having been boiled in a solution of soap, the colour appeared pretty good. 2. The solution of soap became very red, but communicated a very indifferent colour to paper.

M. Merimé, a painter, who seeks to render physical science subservient to his art, has made some interesting experiments on madder, the object of which was to procure a lake uniting durability to lustre. The results of these experiments, which he has communicated to us, may possibly be useful in dyeing.

The pellicle, which serves as a bark to the madder root, was separated from its pulpy and ligneous part, and he obtained from both a lake whose lustre approaches to that of carmine, but which is much more durable when he previously submitted them to immersions and lotions, so as to remove a dun colouring substance. The bark, however, yielded less than the ligneous portion. After the preliminary immersions, he digested them in a feeble solution of sulphate of alumina; after which he precipitated by alkali this solution, which varied in the depth of the shade.

It appears then that madder may be considered as composed of two colouring substances, one of which is dun, (tawny,) and the other is red. Both of these substances may combine with the stuff. It is of consequence, however, to fix only the red part. The dun portion appears to be more soluble, but its fixity on stuffs may possibly be increased by the affinity which it has for the red portion.

The different additions made to madder, and the multiplied processes to which its dye is sometimes exposed, have probably this separation for their chief object.

The red portion of madder is soluble, but in small quantity,

in water. Hence, a limited concentration can be given to its solution. If the proportion of this substance be too much increased, so far from obtaining a greater effect, we merely augment the proportion of the dun part, which is the more soluble of the two.

The red part appears to be especially apt to form the pellicles observed by Watt. De Saussure has shown, that during the formation of these pellicles in the extracts of vegetable substances, for which the contact of air is required, the oxygen gas is changed into carbonic acid; that water is at the same time formed by the more intimate union of the oxygen and hydrogen contained in the substance, and that the residuum thereby gets an excess of carbon; so that in the experiments of Watt these pellicles dissolved but partially, and their solution was brown. The red particles, therefore, lose their solubility, and become brown by ebullition, without the influence of atmospheric air. The cause of this last alteration is not hitherto determined by experiment.

Potash, and carbonate of potash, augment the solubility of the two colouring parts, without accelerating the effect of oxydation; thus, it would seem to be advantageous to add a small quantity of alkali to the madder baths.

The solution of tin affords lakes devoid of lustre, probably because the two species of colouring matters are precipitated together. This mordant, of so great advantage in a great number of dyes, can hardly be useful in those of madder. We shall see, however, that it is capable of heightening the brilliancy of the Adrianople red; but at a period of the operation when the dun part has been removed.

The considerations which we have just now presented, are, in part, nothing but conjectures towards explaining the properties observed in the different processes to which madder is subjected. We suppose, for example, the existence of two species of colouring particles; but these may possibly be derived from a single one, which, by the successive operations that it undergoes, is resolved into two.

## CHAPTER II.

*Of the Processes used in dyeing with Madder.*

Wool would take with madder only a weak and perishable dye, were not the colouring particles fixed by a base, which combines them more intimately with the stuff, and which screens them in part from the destructive action of the air. For the accomplishment of this object, the stuff is, first of all, boiled with alum and tartar, for two or three hours; after which it is drained, slightly wrung, then enclosed in a bag, which is carried into a cool place, and let alone for some days.

The dose of alum and tartar, as also their relative proportions, vary much in different dye-houses. For one pound of wool, Hellot adopts a little less than the third of alum and tartar. If the proportion of tartar be increased to a certain degree, instead of a red, there would be obtained merely a deep, but durable cinnamon colour; because the acids tend, as we have seen, to give a yellow hue to the colouring portion of madder. Poerner diminishes somewhat the proportion of the tartar; of which he prescribes only one-seventh of the alum. Scheffer, on the other hand, prescribes a quantity of tartar double that of alum. But it has been ascertained, that by employing one-half of tartar, the colour inclined more to the cinnamon than when it had been reduced to one-fourth of the alum.

Ebullition must be avoided for the dyeing bath into which merely madder has been put, because at this degree of heat the colouring substance is easily spoiled, and assumes a deeper hue.

When the water is no hotter than the hand can endure, Hellot directs to throw into it one part of the finest *grape* madder for two parts of the wool to be dyed, and to rake well before introducing the wool, which must be kept an hour in it without making the bath to boil; but to render the dye faster, it may be boiled towards the end of the operation for three or four minutes at most. Beckman recommends to add a little alkali to the madder bath.

By this process, reds are obtained which are never so beautiful as those of kermes, and much less so than the lac and cochineal

ones; but as they cost little, they are employed for common stuffs, which could not bear the expense of a dearer dye. The madder reds are occasionally rosed with archil and brazil wood, to make them more beautiful and velvety; but the lustre lent by this means is not lasting.

Poerner, Scheffer, Bergmann, have employed solution of tin in different modes; but our own multiplied experiments do not confirm the advantages of these processes.

Madder does not afford a colour of sufficient brilliancy for dyeing silk, and we conceive it useless to detail the processes which Lafolie, Scheffer, and Giobert have given on this subject.

Madder is employed for dyeing linen and cotton red, and even for giving them several other colours, by means of different mixtures. It is the colouring drug most useful for this kind of dyeing. It is proper, therefore, to show in sufficient detail the different methods by which this dye may be rendered more permanent, beautiful, and diversified in its effects. Linen takes the colour of madder with more difficulty than cotton; but the processes which succeed best with the one, are also preferable for the other.

Two species of madder red on cotton are distinguished; the one called simply madder red, the other, possessing far more lustre, is called Turkey red, or Adrianople red, because it was for a long time obtained from the Levant.

We may also regard as a distinct dye, that employed in calico printing. These three kinds of processes now to be described, may mutually throw light on one another, and serve to determine the most proper means for accomplishing the object of each.

Vogler has tried the effect of a great number of the substances employed as mordants, or in the dyeing bath, and he found that those which produced the best effect were glue, ox-gall, and other animal matters, as sheep's dung. Muriate of soda rendered the colour faster, but more dull. Galling, likewise, procured a richer colour. Other astringents, sumach, and pomegranate rind, for instance, produced a similar effect. A little alkali added to alum improves it. A small quantity of tartar has been useful, but too great a proportion of tartar, as well as of other acids, makes the colour pass to yellow. Different metallic salts produced some variations in the shades and solidity,

but not remarkable enough to deserve notice. In speaking of black, we have detailed the process which Vogler indicates for dyeing cotton black by means of madder. He justly remarks, that drying is useful between each operation, after rinsing the cotton on its quitting the bath. This drying ought to be performed in the shade, especially when alum is employed, because when too much of this is thrown down on the stuff, it crystallizes on its surface. He further remarks, that an ebullition of too long continuance in the madder bath destroys the colour with which the stuff is charged.

In the experiments of Vogler, cotton took the colour always better than thread (linen); the difference, however, was not very great, when the subject was a hempen or woollen cloth, a little worn, and become soft to the touch; and when its texture was very loose, or the yarn was slightly twisted.

Le Pileur d'Apligny gives a very detailed description of the process followed at Rouen, for dyeing cotton red. We shall copy it.

The cotton must be scoured, then galled in the proportion of one part of nut-galls for four of cotton, and lastly alumed at the rate of one of Roman alum for four of cotton, and the same proportion of water. To the solution of alum there is added one-twentieth of a solution of soda, made with half a pound of ordinary soda per  $1\frac{1}{2}$  pints.

Some persons put in one-half less soda, and diminish the water by a sixth, replacing the difference by a solution of tartar and arsenic. Le Pileur d'Apligny considers the last ingredients to be hurtful.

When the cotton has been withdrawn from the mordant, it is gently wrung with the pin, and dried. The more slowly the drying takes place, the more beautiful is the colour. Usually only 22 pounds of cotton are dyed at a time, and it is even more advantageous to dye no more than one half; because, when too many hanks are worked in the copper, it is more difficult to dye them uniformly.

The boiler in which this latter quantity of cotton is dyed, should contain about  $52\frac{1}{2}$  gallons of water. It is to be heated; and when the hand can hardly be suffered in it,  $6\frac{1}{2}$  pounds of good *grape* madder of Holland are to be put in, and carefully distributed through the bath. Whenever it is well mingled, the



cotton is to be plunged into it, hank by hank, previously passed over the sticks, and allowed to rest on the edge of the boiler. The whole cotton having been plunged in the bath, the hanks are worked and turned in succession round every stick, during three quarters of an hour, preserving the bath always at the same degree of heat, without letting it boil. On the expiration of this time, the cotton is lifted up, and withdrawn on the edge of the boiler. About a pint of the soda ley above mentioned, is now poured into the bath. The cotton is again let down into the copper, and is boiled in it for twelve or fifteen minutes. Lastly, it is lifted out, drained, wrung, washed in the river, and wrung a second time on the pin.

After two days a second maddering is given to this cotton, at the rate of one-half its weight of madder, working it in the same way as for the first maddering, only no ley is added, and pit-well water is used for the bath. This maddering being finished, the cotton is allowed to cool, washed, wrung, and dried.

Le Pileur d'Apligny thinks that this method of dyeing at two baths is not beneficial, because it wastes more time and fuel, and because the second maddering cannot afford much dye, the salts of the mordant having been exhausted by the first. He proposes another method, already pursued, he says, with success, by several dyers. It consists in giving two alumings to the cotton, and then dyeing it in a single bath.

To brighten this red, a quantity of tepid water, sufficient to soak the cotton, is put into a boiler or a tub. About a pint of ley is poured over it. The cotton is dipped in this bath, by portions, left there an instant, lifted out, wrung, and dried. According to Le Pileur d'Apligny, this brightening is a useless operation. As the red cotton (yarn) is intended for making cloth, from which the dressing must be partially removed after it is woven, the colour of the cotton is brightened at the same time, by being turned through hot water, quickened with a little ley. On taking them out of this water, these cloths are washed in the river, spread out on the grass, where the red brightens much better than it could do by any other operation.

Wilson rightly prescribes the use of the mordant, known by the name of calico-printers' mordant, which will come under our consideration in dyeing cotton red. By his process, it is requi-

site to gall, dry, impregnate with a mordant diluted with hot water, dry again, madder, wash, and dry.

The mordant employed for producing reds on printed goods, is the acetate of alumina, prepared by the processes already described, and more or less concentrated, according to the intensity of the shade wished to be obtained.

When the goods have undergone the desiccation, which ought always to follow the printing on (of the mordant), they are turned through a boiler, which contains cow dung diffused through water. For the mordants intended for light shades, it is proper not to leave the cloth in it more than five or six minutes, at a gentle heat, not exceeding 133° Fahr. The heat may be increased, and the duration of the dunging, for mordants which are to produce deep colours; but, in all cases, it is to be conducted with great circumspection, because, by pushing it too far, the mordant is removed from the cloth, and by doing it too little, the mordant not combined with the stuff, which lies loosely on it, afterwards impoverishes the dyeing bath, and fixes on the portions of the cloth, which are to remain white, some of the colouring matter that cannot be completely destroyed, without affecting the colour very considerably.

For maddering, the madder is carefully mixed with the hot water of the boiler, immediately after kindling the fire beneath it, and the cloths being attached to each other at their ends, are introduced. They are kept in motion during the whole time that the maddering lasts, so as to be evenly dyed, with which view they are passed round a winch that may be turned by a child. The fire is to be gradually raised, so that the bath be brought into ebullition in three-quarters of an hour, or an hour at farthest. At this period the operation should be stopped the instant that the colours on the cloth have assumed the suitable shade; but if the shades be deep, the maddering may, without inconvenience, be prolonged till the bath becomes dirty, and changes to a tawny hue. In this case, even two madderingings should be given to the cloths, dividing between them the quantity of madder requisite for giving the colour all its intensity; for the colouring matter of the madder is spoiled by ebullition; and by thus prolonging it, as would be necessary were the whole madder employed in a single bath, we should not only fail in

raising the colour, on account of the alteration which the colouring matter experiences, but at a certain term even what had been already fixed on the cloth would be degraded, and thus we should obtain colours which are neither sufficiently deep (strong) nor bright.

By adding a little potash to the madder the moment it is put into the boiler, the solution of the colouring matter is facilitated, and the colours are more speedily raised. The addition of a certain quantity of chalk appears to brighten the colours a little, especially when they are faint: bran is much more efficacious, and ought not to be neglected when light and brilliant hues are wanted. If the madding have been well managed, the white ground may be afterwards restored, by passing a single time through bran, and then exposing on the grass.

Immediately after the madding, the goods are washed and passed into coppers, in which bran is boiled in water; they are laid out on the grass; and these two operations are alternately repeated, till the unprinted parts of the cloth have recovered their whiteness.

The madding of printed goods requires pains and precautions, which long practice alone can teach. The causes which make their effects to vary, are too numerous for us to point them all out here. The quantity of madder employed, the duration of the madding, the manner of managing the fire, are, along with the dunging, the circumstances which have most influence; and they cannot be subjected to any rule, because they must differ more or less in almost every process.

It is plain, that all these operations have for their objects; 1st, to remove the mordant uncombined with the cloth; 2d, to fix the colouring matter; 3d, to carry off, by the action of the air and bran, the dun colouring matter which is mixed with the madder, as well as the colour which covers the parts of the cloth not impregnated with mordant.

The cloths intended for printing ought to be very carefully bleached. The more perfect the white is, the more lustre do the colours take, and the more easy is the unmadding. The fine whites on sale, are not even sufficient; and it is right to give them, at least, one ley, one exposure on the grass, or one immersion in chlorine acid, and to let them also soak some hours

in water acidulated with sulphuric acid. Very frequently, several leys and several immersions must be given. Thus the dressing (paste) is completely removed, the remaining colouring matter of the cloth is destroyed, which, by fixing in a very durable manner that of the madder, might render the unmaddering a difficult operation; and thus also the greater number of the stains formed during the maddering, to which the name of madder spots is given, are prevented.

These stains, almost indelible, very common on certain kinds of cotton cloth, and of a colour perfectly similar to what madder gives to those parts of the cloth impregnated with oil, seem to arise from a combination with grease or oil, analogous to what takes place in the preparations of Turkey red. It is very probable that they are produced by the grease employed in the *parou*, or by the soap which must be employed in bleaching. The combination which in that case may be formed on the stuff, resists the subsequent operations well; and it will be seen, in the process for the Adrianople red, that the action of alkaline solutions, even pretty concentrated, is insufficient to destroy the combination of the oil with the cotton.

A strong ley, run off very hot, does not afford a complete guarantee against these spots, although it may be the surest means of avoiding them. It would be of great consequence for calico printers to be able to exclude from weaving and bleaching both grease and soap.

The Adrianople red has a lustre, which it is difficult to imitate by all the processes hitherto described. It has, besides, the property of resisting more completely the action of the different re-agents, as alkalies, soap, alum, acids. Vogler acknowledges, that by his numerous processes he has not been able to obtain a red possessing a durability equal to that of Adrianople, although he formed one much more permanent than the false Adrianople reds, which are often used for the *siamoises* (coarse cotton cloths) and other red goods.

Aquafortis (dilute nitric acid) is, according to the same author, the surest and most expeditious means for distinguishing the true red of Adrianople from the spurious. It is sufficient to plunge a thread of the latter into it. It is soon seen to grow pale, and in less than a quarter of an hour it becomes white,

whilst the true Adrianople red remains an hour without being affected, and it never loses the colour entirely, which only turns orange.

The Adrianople red, which for a long time came to us through our Levant trade only, stimulated the industry of our artisans; but the attempts were for a long time fruitless, or success was confined to a small number of dyehouses. Abbé Mazaes published experiments which threw much light on this dye; and the government promulgated in 1765, from information that it had procured, an *instruction*, under the title of *Memoir, containing the process for the incarnate cotton red dye of Adrianople on cotton yarn*. The same description is found in the treatise of Le Pileur d'Apligny; but this process has not completely succeeded. It appears that the fault consisted principally in the too great concentration of the alkaline solutions. A mystery is made in the different dyehouses of the changes introduced into the process, by means of which more or less success has been obtained. We shall now give the description which Clerc, who conducted with success a manufacture of this kind at Vaudreuil, communicated to the author of these Elements, and which appears to differ very little from the most usual practice.

*Process of the Adrianople, or Turkey Red.*

LET there be 110 pounds of cotton to dye. We must begin by scouring it well. This operation is performed by boiling the cotton in a copper with a soda ley, at one degree of the areometer of Baumé, ( $1\frac{1}{2}^{\circ}$  Tw.) and there is usually added the remainder of the bath which has served for passing the cottons through *in the white preparation*, (*en l'apprêt blanc*), which is called *sickiou*.

For scouring the cotton properly, and preventing it from entangling, a cord is passed round three hanks, (the hank is composed of four skeins or knots, (*pentes*), which weigh altogether one pound.) It is thrown into the copper when the ley begins to boil. It is carefully immersed, so that it may not be burned upon the sides of the boiler, which should hold about 131 gallons for 110 pounds of cotton. The cotton is perfectly cleansed when it sinks of itself in the copper. It is then taken out and

washed knot by knot in the river. Lastly, it is wrung and stretched out to dry.

*Second Operation.—Dung Bath.*

Put into a tub 110 pounds of Alicant barilla, reduced to coarse powder. This tub must be pierced with a hole near its bottom, that the liquid may run from it into another tub placed beneath. The barilla being in the upper tub, about  $65\frac{1}{2}$  gallons of ley water are poured over it. When the water which is let off into the inferior tub marks two degrees on the hydrometer of the soap boiler, it is fit for the dung bath, which is made in the following way.

From 26 to 33 pounds of sheep's-dung are set to steep in a large earthen vessel, in the ley of two degrees, and it is broken down with a wooden pestle. It is then passed through a hair sieve placed over the vat in which the bath is to be prepared. Into this vat  $13\frac{1}{2}$  pounds olive oil of Provence are poured, stirring well with a rake, in order to mix the oil with the soda ley and the dung. Some of the soda ley is poured over it. There are usually required 32 gallons of water to soak 110 pounds of cotton. When the bath is thus prepared, the cotton is to be passed through it.

For this purpose some of the bath is lifted in a wooden bowl, and poured into an earthen vessel, built at a convenient height for working easily. A hank of cotton yarn is taken and worked well with the hands. It is lifted up several times, turning it about in the vessel, and afterwards hung up on a wooden hook attached to the wall. It is slightly wrung out, and thrown on a table. The same operation is repeated on each hank. The table on which the cotton is thrown should be raised two or three decimetres (about 10 inches) from the ground. A workman takes a hank in each hand, and strikes it on the table to extend the threads. He changes the side (turns it over) three times, afterwards makes a small twist to form a head to the hank, and lays it flat on the table. Not more than three hanks should be put on one another, because too great a load would squeeze the bath out of the under hanks. The cotton must remain on the table 10 or 12 hours; after which it is carried to the stretching, (frames,) in order to be dried.

*Third Operation.—Bath of Oil, or White Bath.*

The ley of soda of two degrees of the hydrometer is taken; and after cleaning thoroughly the tub in which the dung bath stood, there is put into it  $11\frac{1}{2}$  pounds of olive oil, and the soda ley is poured over it, stirring with the rake, (paddle,) in order to incorporate the oil. This bath should resemble thick milk; and when good, the oil must not separate at its surface. Some of this bath is next put into the earthen vessel, and the cotton is turned through it hank by hank, as in the preceding operation. It is thrown upon a table and *creped*, (that is, beat on the table,) and thereafter left upon the table till next day, when it is taken to the stretching to be dried.

*N.B.* About 28 gallons of ley are required for this bath.

*Fourth Operation.—First Salt.*

On the soda sediment in the tub, fresh soda is put, if the water poured over the former has not three degrees. For this operation 28 gallons of soda ley must then be taken, which are poured into the tub over the remainder of the white bath; and the cotton is passed through it as above. This operation is called *giving the first salt*. The soda ley has three degrees.

*Fifth Operation.—Second Salt.*

The cotton is passed through a soda ley of four degrees, with the same mode of working as above.

*Sixth Operation.—Third Salt.*

The cotton is passed through a soda ley of five degrees.

*Seventh Operation.—Fourth Salt.*

The cotton is passed through a soda ley of six degrees; and after being worked with the same pains, it is carried to the stretching to be dried on well-smoothed poles. When the cotton is dry, it is taken to the river to be washed in the following manner.

*Eighth Operation.*

The cotton is to be steeped in water, then withdrawn, and allowed to drain on the horse, (*bayard*.) Water is thrown on it repeatedly, and at the end of an hour it is washed, knot by knot,

to free it thoroughly from the loose oil, a circumstance very essential for its taking the galling well. It is now wrung with the jack and pin, and stretched on the poles to dry. The cotton, when thus washed, should be of a beautiful white.

*Ninth Operation.—Galling.*

For the galling, good nut-galls in sorts (a name known in commerce, the galls in sorts being one-half black galls, and one-half white) should be chosen, and after having bruised them, for 110 pounds of cotton 13½ pounds are to be put into a copper, and boiled with 21 gallons of pure river water. Three hours are commonly required for boiling them well. The decoction is perceived to be properly done when the galls are easily crushed under the fingers like pap. Ten and a half gallons of fresh water are now to be poured in, and the decoction is then to be passed through a very close hair sieve, kneading the pulp in the hands to extract all the resinous substance. When the water is settled and clear, the galling is to be performed in the following manner.

Into an earthen vessel, fixed in the wall at a convenient height for working, from 2 to 2½ gallons of the nut-gall liquor are poured, and the cotton is passed through it hank by hank, squeezing it well with the fists, then wringing it with the pin; and in proportion as this is gone through it is immediately carried to be stretched and dried, an essential precaution, which prevents the cotton from blackening. When the cotton is dry, the aluming is to be performed in the following manner.

*Tenth Operation.—Aluming.*

After thoroughly cleaning the copper, in which the decoction of galls was made, 28 gallons of river water, and 42 pounds of Roman alum are introduced, and dissolved without boiling. When the solution is complete, 1½ gallons of soda ley of five degrees are poured in; and through this, the cotton is passed hank by hank as for the galling. It is afterwards stretched out to dry. It is washed from the alum as follows.

*Eleventh Operation.—Washing from the Alum.*

After having allowed the cotton to steep, and drained it on the horse (*bayard*), each hank is to be three times separately



washed, then wrung with the pin, and taken to the tenter ground.

*Twelfth Operation.—Remounting on the Galls.*  
(*Remonter sur Galle.*)

This operation consists in a repetition of the preceding ones. A white bath is prepared like that described in Article 3; 13 $\frac{3}{4}$  pounds of good fat oil of Provence are put into a tub, and 28 gallons of soda ley are poured over it, of two degrees of the (*pèse-liquor*) *hydrometer* of the soap boilers. Care is taken to stir the bath well, and the cotton is passed through it, as has been described in the 3rd Article.

*Thirteenth Operation.—First Salt.*

The cotton, after being well dried, is passed through a soda ley of three degrees.

*Fourteenth Operation.—Second Salt.*

The cotton being dried, is passed through a soda ley of four degrees.

*Fifteenth Operation.—Third Salt.*

The cotton is passed, when dry, through a soda ley of five degrees, when all the dips are finished. It is now dried, washed, galled, and alumed with the same doses and the same attentions described in Articles 9, 10, and 11. The cotton has then all the necessary preparations for taking the dye well. The cotton, on quitting these preparations, should be of the colour of the bark of a tree. A very essential point to be observed, is to submit the cotton to no dip till it be perfectly dry, without which there would be a risk of the dye being mottled. When the cotton is stretched on the poles, it must be carefully shaken and turned over to dry it uniformly.

*Sixteenth Operation.—Dyeing.*

A copper of an oblong square form is usually employed. It should hold about 87 gallons of water, and at this rate 27 pounds of cotton may be dyed in it at a time. To commence the operation of dyeing, the boiler is to be filled with water to within four or five inches of the top; there is next poured into it a pailful of ox-blood, or sheep's blood, which is better when it

can be had, containing about  $5\frac{1}{2}$  gallons of blood. The *lizari* fine madder is now introduced. When a fine lively striking colour with much body is wanted, several *lizaris* are mixed together; for instance,  $1\frac{1}{2}$  pounds of *lizari* of Provence and  $\frac{1}{2}$  pound *lizari* of Cyprus; or if there be none of Cyprus, equal parts of the *lizari* of Provence, Tripoli, or Smyrna. The dose is always two parts to one of cotton. When the *lizari* is in the copper, it is stirred with a rake to break down any lumps; and whenever the bath is tepid, the cotton stretched on skein sticks, called *lisoirs*, is plunged into it. Two hanks are usually put on each stick. Care should be taken to immerse it well, and that the cotton be turned round the *lisoirs*, end for end, by means of a pointed stick passing between the hanks and the *lisoirs* that the cotton rests upon. This operation lasts an hour; and when the copper begins to boil, the cotton is taken off the *lisoirs*, and plunged into the copper, each hank being suspended by means of a cord passed through its sticks suspended over the copper. The cotton should be kept boiling for about an hour, in order to extract the whole colouring substance of the madder. There is a method besides, of ascertaining when the colour is extracted; for a white froth then forms on the copper. The cotton is now tossed out of the boiler, and washed skein by skein in the river; then it is wrung with the pin, and hung up to dry.

*Seventeenth Operation.—Brightening.*

Into the boiler employed for the scouring, which should be capable of holding 131 gallons of water, soda ley of  $2^{\circ}$  of density is poured, with which it is filled to within 10 or 12 inches of the top. There is next poured in from 4 to  $5\frac{1}{2}$  pounds of oil of olives, and  $6\frac{1}{2}$  pounds of white Marseilles soap sliced very fine. The whole is well stirred till the soap be melted; and when the copper begins to boil, the cotton is introduced, a cord being previously passed through it to prevent its entanglement. The copper is covered up, its lid is stuffed with old linen, loaded, and made to boil with a small fire for four or five hours. The copper is then uncovered, when the cotton should appear finished, and of a beautiful red. The cotton should not be withdrawn from the copper till the end of ten or twelve hours, because it becomes richer in the brightening, and takes more lustre.

It must thereafter be well washed, skein by skein, and dried, when the operation is complete.

I am in the habit of giving my cottons one dip after they are well dried. It consists in making a solution of tin in nitric acid, with 1-16th of sal ammoniac. I dilute this solution with 28 gallons of water, and I pass my cotton through it. It must be afterwards washed. This dip gives a very fine lustre to the cotton.

N.B.—Into the *sickiou* tub only the remainder of the first preparations (*apprêts*) is put. What remains after the cotton has been galled is good for nothing and must be thrown away.

Chaptal, whose researches and enlightened zeal for the advancement of the arts have contributed so much to their progress, has had the kindness to communicate to us the notes which he had collected in his dye-houses, near Montpellier. We have extracted from them the following processes for dyeing Adrianople red, which he has long practised himself with much success.

The first precautions to be taken in this dye, consist in the good choice of materials. The fittest oil for this operation is what comes from the river of Gênes, under the name of dyeing oil. Some is also brought from the south of France. To try these oils, some drops are poured into a glass so as to cover its bottom, and it is filled up with soda ley, marking from 1° to 2° on the areometer of Baumé, (1½° to 3° Tw.) The mixture becomes milky; this soapy liquid is transferred several times from one glass to another, in order to mix it well. It is then left at rest for several hours. The liquor should remain uniformly milky, provided the oil be good; if it separates in little drops, or if the bottom of the liquor assumes the appearance of ill clarified whey, while on the top a pasty zone (*bourlet*) forms, the oil is of bad quality.

The sodas (*barillas*) of Spain, Alicant, or Carthage are to be preferred. In the absence of these, that of Narbonne may be used. Good soda should be very hard, grey outside, blackish in its fracture, difficult to pulverize, and soluble. Such as have effloresced in the air, and in which muriate of soda abounds, cannot be employed for fine colours.

In the operations about to be described, the proportions are given for one portion of cotton weighing 220 pounds.

The cotton is scoured by boiling it in a soda ley, which marks from 1° to 3° on the areometer of Baumé, (1½° to 4° Tw.) For

this purpose, the residues of the sodas employed for the saponaceous emulsions are used. The cotton is known to be completely scoured when it sinks well, and when no hank comes floating up; it is then washed and dried.

To give cotton the first preparations, we prepare a soda ley at  $1^{\circ}$  in a great earthen jar, with about 33 gallons of water. We try if it cuts the oil well, that is to say, if on pouring in a few drops of oil, it mixes well, growing milky, without leaving any little drops at the surface. In a jar of the above size, we mix 22 pounds of oil with one-third of this ley, agitating carefully. Along with the second third, we mix from  $26\frac{1}{2}$  to 29 pounds of the liquor found in the stomach of ruminating animals. This mixture is to be poured into the jar where that of the oil was made, and after adding to it the last third of the ley, we stir again with very great care. For passing the cottons through this saponaceous liquor, some of it is put into smaller jars, and after impregnating the cotton well with it, this is strongly wrung out. In proportion as we drain the jar, we agitate to prevent any separation taking place in the liquor.

The cotton passed through the oil remains piled up in a heap till next day, when it is taken to the tenter poles. As soon as it is dry, it is passed through a weak ley of soda, which has been mixed with the small residue of the soapy liquid; and it is in like manner left in a heap till it be carried next day to the drying. It is passed, when dry, through a second ley a little stronger than the preceding.

The second soapy liquor is prepared with the same precautions as the first. There is employed for it the same quantity of ley, marking from  $1^{\circ}$  to  $2^{\circ}$ , and about  $17\frac{1}{2}$  pounds of oil, but no animal liquor is mixed with it. When the cotton is passed through this second oil, 44 pounds of soda are added to the 33 pounds previously used. The cotton is passed three or four times through the leys of this soda, taking the precaution of increasing each time the strength of the ley by half a degree, so that the last shall mark nearly  $3^{\circ}$  or  $4^{\circ}$  of Baumé. ( $5^{\circ}$  to  $6\frac{1}{4}^{\circ}$  Tw.)

In this operation potash may be substituted for soda. The cotton takes in fact a wine colour, but it loses this hue in the brightenings.

To prepare the cotton well for the galling and the aluming, it must be washed and dried. The galling bath is prepared, by

boiling 22 pounds of sorted galls in powder with about 22 gallons of water, in which. 33 pounds of sumach have been previously boiled. After half an hour's boiling, 11 gallons of cold water are poured into the copper, that the bath may be large enough for all the cotton to be passed through it. The cotton is dipped in as soon as the heat of the bath permits, and in the same manner as in the soapy liquor. It is then taken to the tenter poles.

The galling is one of the most delicate operations. It is of consequence to impregnate, wring out, and dry the cotton very equally, as well as to dry it neither too slowly, nor in too moist an air, because the parts of the cotton that suffer the action of the air most, blacken, while the others remain of a white-grey. This produces inequalities.

As soon as the galling is dry, the cotton is alumed. With this view, 33 pounds of reddish Levantine alum, or  $27\frac{1}{2}$  of Roman alum, are dissolved in 22 gallons of water. Whenever the solution is completed, about 11 gallons of cold water are poured into the copper, and as soon as the solution acquires a gentle warmth, much below that of the galls, the cottons are passed through it, and dried.

The alumed cotton should be thoroughly washed before proceeding to the other operations. Whenever it is well washed and dry, it is passed through one oil and three leys. The saponeous liquor is prepared with 15 to  $17\frac{1}{2}$  pounds of oil, and the ley of the remainder of the sodas, which have served for the first preparations, which marks, as in the first, only from 1 to 2 degrees.

Thirty-three pounds of soda are now added to the jar, and the first ley is given at 3 degrees, raising each of the succeeding ones by half a degree, so that the strongest shall stand at from 4 to 5 degrees. After the third ley, it is washed and galled in a bath of  $16\frac{1}{2}$  pounds of galls, without sumach. The aluming is made with 22 pounds of Roman alum; after which it is powerfully washed and dried. All these operations must be conducted with the same pains as the first.

In order to have a very uniform colour, 4 pounds of madder must be employed for every 2 pounds of cotton. With this madder 1 pound of sheep's blood is mixed for every 2 pounds of cotton, and it is put into the bath whenever it is tepid. The

cotton is turned in for an hour. When it is boiled for an equal time, it is withdrawn, and washed. It is now of a deep red, or bullock's blood colour. If the blood have not been intermingled, the colour is not so lively, nor so rich, although it be durable; and by substituting for it glue and other animal products, no such agreeable colour is obtained.

The colour of the cotton, after the maddering, is so dull and dark, that it could not be employed in this condition. It is cleared up, or lustre is given it by the *brightening*, and by solution of tin, which the workmen call the *secret*.

The brightening consists in boiling the cotton, for 6 or 7 hours, in the ley of 66 pounds of soda, marking  $2^{\circ}$ , to which 17 to 20 pounds of soap are added. The cotton is not put into the copper till the liquid be boiling hot. The copper is carefully covered, leaving but a small outlet for the steam, and the lid is strongly fastened down, that it may not be lifted up by the compressed vapour. The duration of the ebullition varies according to the intensity of the colour of the cotton, and the strength of the ley employed. When the cotton is thought to be sufficiently brightened, the fire is stopped, the brightening (copper) is uncovered, and a hank is pulled out with an iron hook. If, after washing it well, the colour appears brilliant, and has not any black tint, or if some parts of the cotton begin to be impoverished, the copper is filled up with fresh water, and a stopcock is opened to run it off. Thus the cotton is washed, and is then left in the boiler till next day. It is now washed and dried.

In this condition, the cotton is of a fine colour; but it receives more lustre by the *secret*.

The solution of tin is prepared with pure nitric acid, marking  $32^{\circ}$ . 465 grs. of sal ammoniac are dissolved in the cold, in every pound of acid. When the solution is made, the tin is introduced in small rods, in the proportion of 465 grs. to the pound. It dissolves readily, and the liquor becomes opalescent. Tin is added even till this hue is perceived, which indicates that the acid can dissolve no more.  $16\frac{1}{2}$  pounds of this solution are poured on a solution, somewhat tepid, of  $6\frac{1}{2}$  pounds of Roman alum, put into a large jar. In proportion as the solution of tin is poured into that of alum, the mixture grows turbid and white; at this time the cotton is passed through it with pressure, as usual. It is washed as it passes through.

The mixture of the two solutions should be capable of causing effervescence with calcareous earth, otherwise it will not brighten the colour properly. More or less solution of tin is employed, as the colour is to be more or less deep.

The lustre of the cotton may be further increased, by reviving it with an ebullition of 4 or 6 hours in a solution of from  $17\frac{1}{2}$  to 22 pounds of soap.

Linen yarn takes a colour almost as brilliant as that of cotton, but it must be passed through a double number of oils and leys. The latter must be even very strong, otherwise the oil flows out on the surface. The greatest attention must be bestowed on the scouring at first; for the yarn mingles and entangles by the heat, to such a degree that it can be neither dipped nor unravelled.

A very beautiful red is also obtained by limiting the galling and aluming to a single time, after the three oilings; and by observing to increase the doses of gall-nuts and alum a little.

By the following method we procure red colours, beautiful and permanent, without employing ley, oil, or galls.

Lime slaked in the air is to be dissolved in cold acetic acid. The solution marks from  $5^{\circ}$  to  $6^{\circ}$ ; and it is reduced to  $2^{\circ}$  by the addition of water. Equal parts of this solution and acetate of alumina are mixed. The latter is prepared by pouring 11 pounds of acetate of lead into a solution of 44 pounds of alum for 38 gallons of water. The above mixture is made tepid, and the cottons, merely scoured with care, are passed through it. They are dried, thoroughly washed, dried and maddered with  $1\frac{1}{2}$  pound of madder for 2 pounds of cotton. They are brightened with ley and soap, then passed through a solution of tin, and revived with soap alone, in the proportion of 26 pounds of soap for 220 pounds of cotton.

Very durable reds may be had by passing the cotton through this mordant, after having submitted it to oiling without galling. They are even very deep. But on passing the cotton which has received a single oil and four leys, through a mixture of acetate of alumina, with 1-4th, 1-12th or 1-18 of lime, various very lively shades are obtained.

For making a dead red without lustre, termed in some places, burned red, or Indian red, on account of its resemblance to that of Indian handkerchiefs, the cotton is scoured, boiled for half

an hour in lime water, passed through an oil mixed with some intestinal liquor, and through three leys. It is washed well and turned through a mordant composed of a tepid solution of  $27\frac{1}{2}$  pounds of alum, to which 9 pounds of acetate of lead have been added; and a moment afterwards, 1 pound of soda in powder and half-a pound of sal ammoniac. It is washed with care, and maddered with its own weight of madder. If the colour be poor, it is passed once more through an oil, two leys, the same mordant, and a maddering. It may be brightened with soda and soap. The lime alone produces the difference between this colour and the preceding. It renders the colours more permanent, but duller.

The durable rose (colour) is produced by taking cotton passed through the oils, and which has received more numerous but weaker leys. It is galled with a ley of sumach, in which  $5\frac{1}{2}$  pounds of gall-nuts have been boiled; and alumed with  $38\frac{1}{2}$  pounds of alum. It is now washed, dyed with madder of the best quality, the madder bath being whitened (*blanchi*) with 4 pounds of the oxyde of tin, that precipitates from the solution of this metal in nitric acid. It is brightened with weak ley and soap, dried, passed through a liquor formed of a solution of tin (in nitric acid at  $32^{\circ}$ , diluted with an equal volume of water), reduced to  $4^{\circ}$ . It is now washed and brightened in a solution of 33 pounds of soap, till the colour be rosed in perfection.

On passing the cotton through soap of wool made with soda, taking the same pains as with the soapy liquor prepared for the red, and using very weak leys in the interval, then washing the cotton, and treating it by the same process as for dyeing wool scarlet, it assumes a scarlet tint, paler than that of wool, but pretty brilliant.

Cotton died red may, moreover, be made to pass through all the shades, down to the palest orange. For this purpose, pure nitric acid is diluted with 3-5ths of water; chips of tin are oxydized in it till the liquor grows opalescent, and the solution is employed, at different strengths, from  $2^{\circ}$  to  $20^{\circ}$ . The colour varies according to the concentration of this solution. When it is from  $16^{\circ}$  to  $20$ , shades are obtained which have some relation to those of scarlet.

In general, when brilliant colours are desired, we must not charge them too much with oil; we must give feeble leys long



repeated, charge little with alum, employ the best madders, and, at last, brighten powerfully, without sparing the soap.

Chaptal \* has expounded the principles on which are founded the multiplied operations of the Adrianople red dye, one of great importance in itself, and whose processes may have to a certain extent several useful applications.

He shows, that all these operations have for their object a triple combination; the first, that of the oil with the stuff; the second, that of the tanning with the former; the third, that of the alumina with the preceding two. To this triple combination there is lastly added, that of the colouring substance of the madder. Its dun portion is separated by the brightening, and the lustre of the red portion is increased by a judicious application of the solution of tin.

The oil must be brought into a disposition to combine with the stuff. For this purpose, solubility in water is communicated to it by means of soda; but the oil must be slightly retained by the alkali. Hence, merely a weak solution of soda should be employed, leaving the oil predominant, in order that the alkali may not seize it, and separate it from the stuff.

The oil, to be fit for combining with the stuff, must not be a *fine oil*; but it should have a tendency to form a solid combination; which is undoubtedly indicated, when it is said, *it should contain a strong portion of extractive principle*.

Gall-nuts have an advantage over the other astringents, because the gallic acid, tending to combine with the alkali retained by the stuff, favours the more intimate combination of the oil with the stuff and the tannin.

Chaptal observes, on this occasion, that we may observe a combination of oil with tannin, on mixing a decoction of nut-galls with a solution of soap. It is of consequence to make this combination in due proportions; for if the astringent predominates it grows black; if it be in too small quantity, the colour becomes too weak.

When sulphate of iron, or acetate of alumina, is mixed with a decoction of gall-nuts, a greyish precipitate is formed; in like manner, galled cotton becomes grey the instant that it is plunged into an aluminous solution. Too hot a solution must be avoided,

\*. Mémoires de l'institut. vol. ii.

because a portion of the astringent is dissolved, which would impoverish the colour.

Haussman\* employed, with success, solution of alumina in alkali. To obtain this solution, he precipitated the alumina of sulphate of alumina by caustic potash, of which he added such a quantity, that all the precipitate first formed was redissolved; to this solution he added 1-33d of linseed oil, which formed a liquor having the appearance of milk. As the oil separates with standing some time, the liquor must be agitated before using it. The hanks of cotton, as also those of linen yarn, should be successively steeped in it, evenly wrung out, and dried in the shade for 24 hours. After this they are washed, and the operation is renewed. Two impregnations are sufficient for obtaining a fine red, but by means of a third and a fourth, very brilliant colours may be produced.

The intensity of the red depends on the quantity of madder employed in the dye; with a weight equal to the hanks, the colour becomes rose by brightening; with four times the weight the finest red is produced. The author prescribes the addition of carbonate of lime to the madder, always when the water made use of naturally contains none. Its effect is to decompose the sulphate of magnesia, which Bertholdi found in madder; provided the carbonate of lime can decompose the sulphate of magnesia, and if it be more advantageous to have sulphate of lime than sulphate of magnesia present.

He employs for the brightening, water alone, containing a small bag of bran, keeping up the ebullition for eight hours, and replacing what evaporates.

A great variety of different shades may be procured, by giving another colour to cotton before passing it through the oil bath.

Pallas relates, in the *Journal of Petersburg* for 1776, that the Armenians, whom the troubles of Persia obliged to retire to Astracan, dye Turkey red by impregnating cotton with fish oil, and drying it alternately during seven days; that they have remarked that the other oils would not succeed; that they did not take indifferently the oil of every fish, but chose that of certain fish, which becomes milky whenever an alkaline solution is mixed with it. After these repeated impregnations and de-

\* *Annal. de chim.* tom. xli.

siccations, they wash the cotton, and dry it. They give it then an astringent bath, into which they put a little alum. They dye it in a bath of madder, with the addition of calf's blood. Lastly, they digest it for 24 hours in a solution of soda.

If cotton dyed with madder, by any process whatsoever, be boiled for some minutes in soap water, it assumes a rose colour. If it be then squeezed, a fat matter is expressed from it, which has the colour of Adrianople red, and which fixes itself on white cotton. Etinger observed, in 1764,\* that oil had the property of dissolving the colouring part of the Adrianople red, so that, if it be moistened with oil, its colour is communicable to white cotton when rubbed with it for some time. He thence concluded, that oil must enter into the preparation of the Adrianople red; and the Abbé Mazeas had proved long ago, that oil was indispensable to this dye.†

The species of madder employed has a great influence on the colour obtained. It appears indispensable, for procuring a colour equal to the Adrianople red, to employ the kind called *lizari*.

We should distinguish, in madder-dyed cotton, between the faculty of resisting, for a long time, the action of air, and that of resisting alkalies and soap. The last can only be obtained by means of oils and fats; but the first depends chiefly on the mordants that are used, and the other manipulations. Thus, the reds on printed stuffs may be very permanent, without supporting the action of leys, as the red of Adrianople does.

It is therefore right, independently of the beauty of the colour, to employ processes analogous to that of Adrianople, for such stuffs as are to be exposed to leying, and to frequent washing with soap. (NOTE I I.)

\* Dissertatio de viribus radices rubie tinctorum antiarchitice a virtute ossa animalium vivorum tingendi non pindendibus.

† Recherches sur la cause physique de l'adherence de la couleur rouge, &c. Mem. des savans etrangers, tom. iv.

## CHAPTER III.

*Of Cochineal.*

COCHINEAL was taken at first for a grain, but the observations of Lewinhoek showed that it was an insect. It is brought to us from Mexico. This insect lives there on different species of *opuntia*. The female has the body flattened on the side of the belly, and hemispherical on the back, which is marked with transverse wrinkles. Its skin is of a dull brown. Its mouth is an awl-shaped point which issues from the cavity of the thorax. It has six very short brown feet, and no wings. The male has the body much elongated, of a deep red colour, covered with two wings, extending horizontally, and crossing a little on the back. It has two small antennæ at the head, and six feet, larger than those of the female. Its flight is not continuous, but it flutters about, hopping very rarely. Its life is only one month in duration, and ends with its amours. The fecundated female lives a month longer, dying after parturition. It is sometimes oviparous, and sometimes viviparous. After their birth the young females disperse themselves on the joints of the *opuntia*, where they fix themselves by their proboscis till the end of their lives.

Two sorts of cochineal are gathered in Mexico. The wild cochineal, called by the Spanish name *grana silvestra*, and the fine cochineal, or *grana fina*, termed also *mèsteque*, from the name of a province of Mexico, and which is bred on the *nopal*. The first is smaller, and covered with a cottony down, which increases its weight with a matter useless in dyeing; it yields, therefore, in equal weight, less colour, and is of inferior price to that of the fine cochineal. But these disadvantages are perhaps compensated by its being reared more easily, and less expensively; and by the effects of its down, which enables it better to resist rain and storms.

The wild cochineal, when it is bred on the *nopal*, loses in part the tenacity and quantity of its cotton, and acquires a size double of what it has on the other *opuntias*. It may therefore be hoped, that it will be improved by persevering care in the

rearing of it, when it will approach more and more to fine cochineal.

Thieri de Menonville exposed himself to the greatest dangers in going to observe the breeding of the cochineal at Mexico, in order to carry away this precious production, and enrich the colony of St. Domingo with it. He brought back with him some of the fine cochineal, of the wild cochineal, and of the nopals, which are the species of opuntia best adapted for nourishing these insects.

On his return, he occupied himself with the cultivation of the nopal, the different species of opuntia, and the rearing of the two cochineals; but death suddenly cut him off, and the fine cochineal soon perished. On his return he had observed the wild cochineal on a species of opuntia named *pereskia*, or *patte de tortue*, which is found at St. Domingo. This discovery did not remain unproductive. Bruley engaged with success in the rearing of this cochineal. The circle *des Philadelphes* employed themselves on it, and published a posthumous work of Thieri de Menonville, in which very detailed instructions are given relative to the cultivation of the nopal, and the other opuntias which may be substituted for it with more or less success; as also the rearing of the cochineal, and its preparation.\*

Two months after the mothers kept in reserve have been sown on the nopal, some young cochineals are seen to issue from them. This is the moment when the crop should be gathered. They are killed in boiling water. The plates of hot iron, and the stoves occasionally employed, may deteriorate the cochineals by too great a heat. After they are taken out of the water, they are carefully dried in open sunshine. They lose nearly two-thirds of their weight in the desiccation.

When the fine cochineal is dry, it is to be passed through a sieve large enough to let it go through, but capable of stopping the passage of the *bourres* (downs) and cotton of the larvæ of the males. The *bourres* (coarse downs) are put by themselves, and sold separately, or along with the wild cochineal.

The fine cochineal, when well dried and well preserved, should

\* *Traité de la culture du nopal, et de l'éducation de la cochenille dans les colonies Françaises de l'Amérique, précédé d'un voyage à Guaxaca, par M. Thieri de Menonville. Ann. de chim. tom. v.*

have a grey colour, bordering on purple. The grey is owing to the powder, which naturally covers it, and of which a little adheres. The purple shade arises from the colour extracted by the water in which they were killed.

Cochineal keeps for a long time in a dry place. Hellot says that he has tried some 130 years old, which produced the same effect as new cochineal.

It has been pretty generally believed, that cochineal owed its colour to the nopal on which it lives, the fruits of which are red. But Thieri de Menonville observes, that the juice which serves for its nourishment is greenish; and that it can live and breed on a species of opuntia whose fruit is not red.

The decoction of cochineal is of a crimson hue, inclining to violet.

A small quantity of sulphuric acid caused this liquor to assume a red colour verging on yellow; and a little precipitate, of a fine red colour, was formed.

The solution of tartar changed the liquor to a yellowish-red. A slight pale red precipitate is slowly formed. The supernatant liquid remained yellow; on pouring into it a little alkali, it took a purple hue. The alkali quickly dissolved the small precipitate, and the solution was purple. Solution of tin formed a rose precipitate with the yellow liquor.

Solution of alum cleared up the colour of the infusion, giving it a redder tint. A crimson precipitate fell, and the supernatant liquid retained a crimson colour, slightly reddish.

The mixture of alum and tartar produced a brighter colour, more lively, inclining to yellowish-red. A much less abundant precipitate was formed, and much paler than in the preceding experiment.

The solution of tin formed a copious deposit, of a beautiful red. The supernatant liquid was clear, and did not change colour on the affusion of alkali.

Having poured in the solution of tartar, and afterwards the solution of tin, there was formed, more speedily than in the preceding experiment, a rose deposit, verging on lilac; and although a superabundance of the tin solution was added, the supernatant liquor remained a little yellow.

The solution of muriate of soda rendered the colour a little deeper, without making the liquor turbid.

Muriate of ammonia gave a shade of purple without causing a precipitate.

Sulphate of soda produced no sensible change in the liquor.

Having boiled a little cochineal with half its weight of tartar, the liquor inclined more to the red, and had a much deeper colour than that proceeding from an equal quantity of cochineal without tartar; but the first yielded, with the solution of tin, a much more abundant precipitate, which had a more intense colour, so that the tartar promotes the solution of the colouring particles of the cochineal. Although the colour of the solution be less deep, the precipitate derived from it by the solution of tin has a livelier hue.

Sulphate of iron formed a brown-violet precipitate, and the supernatant liquor remained clear, with a dead-leaf cast (*feuille morte*).

Sulphate of zinc caused a precipitate of a deep violet; the supernatant liquor remained clear and colourless.

Acetate of lead afforded a purple-violet precipitate, not so deep as the preceding; the supernatant liquor remained clear.

Sulphate of copper produced a violet deposite, which formed slowly; the supernatant liquor continued clear and violet.

If alcohol be digested on the extract which the decoction of cochineal yields by evaporation, the colouring particles dissolve, leaving a residuum, which retains merely a colour of wine lees, not removable by fresh alcohol. This portion affords, in the analysis by fire, the products of animal substances.

The alcoholic tincture of cochineal leaves, on evaporation, a transparent residuum of a deep red, which, when dry, has the appearance of a resin. It yields also, by distillation, the products of animal substances. Hence the colouring matter is an animal substance.

The cochineal *mèsteque* was compared to the wild cochineal of Mexico, and that reared in St. Domingo, and transmitted by Bruley.

The decoction of the wild cochineal has the same hue as that of the cochineal of St. Domingo. This shade borders more on the crimson than that of the cochineal *mèsteque*; but the precipitates that are obtained, whether by solution of tin or of alum, are of a colour perfectly equal to those of the *mèsteque* cochineal;

and it is these precipitates which colour stuffs by combining with them.

Chlorine was had recourse to for determining the proportion of the colouring particles which the decoctions of the different cochineals contained. An equal weight of each of the three cochineals was boiled for an hour, rendering all the circumstances as equal as possible. These three decoctions being filtered, were poured each into a graduated glass cylinder, and some of the same chlorine was mixed with them, till they were all brought to the same shade of yellow. The quantities of acid, which represent the proportions of the colouring parts, were found to be nearly in the ratios of the following numbers: eight for the cochineal of St. Domingo; eleven for the wild cochineal of commerce; eighteen for the mesteque cochineal.

We therefore perceive, that the cochineal of St. Domingo is not only very inferior to the mesteque cochineal, but to even the wild cochineal of Mexico; and in fact it is much more cottony, and smaller; but these disadvantages should not diminish the zeal of those who are engaged in rearing it.

The observations of Thieri de Menonville have already proved, that the wild cochineal lost its cotton, and became larger by a succession of well nursed generations; and, at the beginning, nopsals which had not attained the requisite size, were necessarily employed.

In reference to the quality of the colour, it has been seen that the cochineal of St. Domingo did not yield to the mesteque cochineal; but if the cotton with which it is covered should, in the operations on the great scale, injure the beauty of the scarlet, whose lustre is so easily affected, a more advantageous employment could be found for it, either for half scarlets, or for crimsons, and the other shades which are less delicate than that most lively of colours. Wild cochineal is found in several parts of North America; Dr. Garden observed it in South Carolina and in Georgia. It exists also in Jamaica, and some might possibly be found equal to that of Mexico. Bancroft examined some of it that came from the Brazils, and obtained a colour equal in beauty to that of the mesteque cochineal. It yielded half the quantity.

Anderson imagined, that he had found wild cochineal at Madras; but the hopes which he excited have not been realized.



The insect which he mistook for the cochineal, seems, according to Bancroft, to approach to the kermes; and the trials which he made on a sample sent to him, showed that this insect could give stuffs only a chocolate brown colour, but one indeed very durable.

A distinctive character may be observed between cochineal and madder, in their mode of comporting themselves with reagents: both receive a yellow colour from the acids; but if the colouring particles of the cochineal be separated by a substance that precipitates them from the acid liquor, they reappear with their natural colour little changed; whereas those of madder retain a yellow or tawny hue. Hence the mordants which possess a redundant acid, such as the solution of tin, are employed much more successfully with cochineal than with madder. This effect is probably owing to the combination of the colouring part of the madder with the oxyde of tin retaining a portion of acid, while that of the colouring part of cochineal retains none, or much less. (NOTE KK.)

Carmine is the lake obtained from cochineal, by means of alum; but with the cochineal is blended a certain proportion of *autour*, a bark which comes from the Levánt, of a paler colour than cinnamon. *Chouan* is also commonly added. It is a yellowish-green seed of an unknown plant, which also comes from the Levant. It would seem that these two substances furnish, along with alum, a yellow precipitate, which serves to brighten up the colour of the cochineal lake in the same way as a yellow colouring matter serves to give scarlet a flame colour. A superior carmine is at present made by a process which is not promulgated. Carmine was formerly prepared with kermes, whence it takes its name. (NOTE LL.)

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## CHAPTER IV.

### *Of Dyeing Scarlet.*

SCARLET is the most beautiful and the most brilliant colour among dyes. Taste fluctuates with regard to the shade in demand. Sometimes scarlet is sought for of a perfect and deeper red; more frequently inclining more or less to the colour of flame.

We cannot expect to obtain the desired shade from the precise doses prescribed in the processes, from variations in the quantity of the colouring particles contained in the different kinds of fine cochineal, and particularly from the solutions of tin that are used differing considerably from each other; but the just proportions of the ingredients to be employed may be readily determined by trials in the small way, so as to obtain the shade called for; and if the pieces which are dyed be above or below this shade, it is not difficult to find the suitable proportions.

The dyeing of scarlet is performed at two operations; the first is called the boiling (*bouillon*), the second the *reddening*.

For a boiling intended to dye 110 pounds of cloth,  $6\frac{1}{2}$  pounds of tartar are thrown into water, a little more than lukewarm. The bath is strongly raked up, and when it is a little hotter,  $1\frac{1}{2}$  pound of cochineal in powder is thrown in, and very well mixed. An instant afterwards,  $5\frac{1}{2}$  pounds of a very clear solution of tin are poured in, which are carefully mingled; and whenever the bath begins to boil, the cloth is introduced, and made to circulate rapidly round for two or three turns; the motion is then slackened. After two hours of ebullition, it is lifted, aired, and carried to the river to be well washed.

For preparing the second bath, which is the *reddening*, the boiler is emptied. When this bath of water is about to boil, 6 pounds of powdered and sifted cochineal are put into it. This is mixed with care, and the stirring being over, when the crust, which spontaneously forms on its surface, opens of itself in several places, about fifteen pounds of solution of tin are poured in. If, after this, the bath rises above the edge of the boiler, it is refreshed (cooled down) by putting in some cold water.

When the solution is well mixed through the bath, the cloth is thrown in, with the precaution of whirling it rapidly for the first two or three turns. It is boiled for an hour, pressing it down into the bath with rods whenever the agitation raises it up. It is now taken out, aired, cooled, then washed in the river, and dried.

The proportions of cochineal and solution of tin which enter either into the *bouillon* or *reddening*, are not uniform. There are dyers who, from Hellot's account, succeed very well by putting two-thirds of the composition and one-fourth of the

cochineal in the *bouillon*, and the other third of the composition and the three-fourths of the cochineal into the *reddening*. Hellot asserts also, that it is not injurious to employ tartar in the reddening, provided no more of it be used than one-half the weight of the cochineal; and it appeared to him to render the colour even more durable. This is actually the practice of some dyers. It has been seen to promote the solution of the colouring particles, an effect which particularly takes place when it is ground along with the cochineal; and by this means the residuum is found to be better exhausted. This consideration has less weight when the work is consecutive, because then the colouring particles present in the residuum are employed in the subsequent operations; but it is proper not to neglect the influence of the tartar on the quality of the colour, which we shall determine more particularly.

There are some dyers who do not lift the cloth out of the *bouillon*, but only refresh this, in order to make the *reddening* in the same bath, by pouring in the infusion of the cochineal prepared by itself, and to which they have added the proper quantity of the composition. Time and fuel are thereby saved, and a good scarlet may be obtained.

As it is usually desired that the scarlet should have much vivacity, approaching to a flame colour, a yellowish tint is given it, by boiling fustet in the first bath, or indeed by adding a little curcuma to the cochineal. The employment of these ingredients may be discovered on cutting the scarlet cloth, its interior being in this case dyed yellow; for, by the ordinary process, the cochineal does not penetrate into the inside of the scarlet, but leaves it white, when it is said to cut.

In the scarlet dye, it is advantageous to use a boiler of tin, because the acid employed attacks copper, whose solution might injure the beauty of the colour. However, as these boilers are difficult to make of a certain size, and as they are liable to be melted, if the fire be not withdrawn before they are emptied, several dyers use copper boilers. But care must be taken to keep them very clean, not to let the acid liquor remain in them, and to prevent the cloth touching the metal, either by means of a network, or an open wicker-work basket.\*

\* A piece of tin lying in the boiler, and in contact with it, will render the copper negatively electrical, and thus prevent the copper from being attacked.—T.

Scheffer prescribes for the *bouillon*, one part of solution of tin, for ten parts by weight of cloth, with an equal quantity of starch and tartar as of solution. He remarks, that the starch tends to make the colour more uniform, and he recommends to throw into the water, when it boils, 1-128th of cochineal; to agitate well; to let the wool boil in it for an hour, and then to wash it. He prescribes next, the boiling for half-an-hour in the bath, which serves for the *reddening*, with 1-32d of starch, 1-24th of solution of tin, 1-32d of tartar, and 1-18th of cochineal.

It appears, that Scheffer employs a much smaller quantity of solution of tin than Hellot; but what he does employ contains much more tin.

Poerner describes three principal processes, according as the shade is to be more or less deep, or more or less of an orange hue, which he wishes to give to the scarlet. He varies the proportions of the solution of tin, of cochineal, and tartar, or omits the last ingredient.

For conducting the process of the scarlet dye in the most beneficial manner, and for varying its results, according to the end in view, the effect of each of the ingredients employed in it must be ascertained.

In the first edition of these Elements, the property of giving a deeper and more rosy hue to the colouring particles of the cochineal had been attributed to the tartar. This opinion might be regarded even as the general one; but Bancroft has justly called it in question. He states that if the tartar be left out, the colour is a crimson; that the tartar gives rise to an insoluble tartrate of tin, which forms with cochineal a yellow colour; that the ordinary scarlet is a mixture of one-fourth of this yellow colour, and three-fourths, or a little more, of the crimson colour, which cochineal gives with the solution of tin. Consequently, he proposes to substitute for the tartar, a preliminary dye, with quercitron, which, by its yellow, produces the same effect, and to dye afterwards with solution of tin and cochineal, of which, in this case, no more than four-fifths of the ordinary proportion are required.

We have dyed scarlet, by employing the proportions of solutions of tin and tartar which have been pointed out, in the first place; in another pattern, we doubled the proportions of tartar; and in a

third, we left out this ingredient. The first took a beautiful scarlet colour; the second inclined more to yellow; and the third had a vinous colour, and was less lively, although not exactly crimson.

It is true, therefore, that tartar causes the colour of cochineal to incline to yellow, and that it produces more of this effect, the greater its proportion. We have not determined, whether this effect may be entirely supplied by a yellow produced by other means. If the proportion of the solution of tin is too great, it becomes prejudicial, and impoverishes the colour, because a portion of the colouring matter is retained in solution. But the different proportions of tin which this solution contains have also some influence. It has appeared to us, in general, that the larger the proportion of tin, the deeper was the colour. We have been sufficiently diffuse on the preparation of the solution of tin, PART I., Section V.

Bancroft recommends a solution of one part of tin, made in a mixture of a little more than two parts of sulphuric acid, and of three of muriatic. He relates several other attempts which he has made, both by dissolving tin in different acids, and by substituting other salts of an earthy and metallic base for the solution of tin. But these attempts do not point out applications sufficiently useful to the art for us to detail their results.

Experience shows, that scarlet may be dyed by a single operation; but an uniform dye is better ensured by dividing it into two operations, when the dyeing is on the large scale. This is not the case with the lighter shades.

If the scarlet just dyed be too much of an orange cast, this may be weakened by washing it in hot water, especially if the water contains some salt with an earthy base.

The *reddening* (bath) which has served for dyeing the scarlet, is not exhausted of its colouring particles, but contains still a quantity, which varies, in proportion as the cochineal has been reduced to a powder of greater or less fineness, and according to the length of ebullition which it has suffered. This bath contains, moreover, a portion of the mordants put into it; but as the nature of this residuum is not uniform, it would be illusory to prescribe the precise doses of the ingredients that should be added for obtaining the shades that may be sought from it. Practice in the same process, and experience, easily guide an

intelligent dyer. We shall therefore confine ourselves to some general considerations.

If much cloth is to be dyed scarlet, we may use for the *bouillon* a *reddening* which has been just employed for dyeing, subtracting from the ordinary quantity of cochineal what may be supposed to remain in the bath, and diminishing likewise the amount of solution of tin. But if a flame colour be wanted, we should begin by boiling a bag of fustet, withdrawing it before we add the other ingredients.

This bath may then be used, as soon as the cloth is taken out, for making pomegranate colour, by boiling a bag of fustet in it. That (the fustet) which has already passed through a bath, is fitter for this shade than what is fresh. After withdrawing it, some tartar and composition are thrown into the bath. It is to be well stirred with the rake, and the cloth must be treated as for the scarlet dye.

In the sequel of this colour the bath may serve for capuchin colours, (*les capucines*), by boiling fustet in it, with the addition of tartar, and solution of tin.

The preceding *bouillon* may likewise be used for lobster-red, orange, gooseberry, golden, and jonquille colours, by boiling fustet in it, adding a little cochineal, and more or less solution of tin and tartar.

When the *bouillon* has been given to all the cloths that are to be dyed, proceeding from the deepest to the lightest colour, they are passed through the *reddening*, advancing, contrariwise, from the lightest to the deepest colour, adding always more and more cochineal and solution of tin, till the pomegranate and flame colours be attained. When it is come to the turn of the golden and jonquille hues, fustet is added, unless these colours have been finished in the first bath, as we shall see may be done for certain shades. For gold and gooseberry colour, a little madder is added.

The colours of gold, gooseberry, jonquille, and chamois, may be made after the scarlet *bouillon*, by adding for the first two, fustet, solution of tin, and a little madder; and a little more fustet, and a little less solution of tin, for the gold colour than for the gooseberry. Much less solution of tin is needed for the chamois (buff). Hind colour (*couleur de biche*) may be made in the sequel of a scarlet *bouillon* without any addition. The coffee

with milk colour (*café au lait*) requires a little fustet and solution of tin, with a very small quantity of madder. To the last ingredients, a little cochineal and tartar are added for the chocolate with milk colour.

A fresh bath is usually had recourse to for the *bouillon* of the cherry colours; and it is composed of tartar and solution of tin. For dyeing them, thereafter, a *reddening* is employed which has served for scarlet, adding to it tartar, solution of tin, and a little cochineal. For the *bouillon* and the *reddening* only half the time is taken that is employed in the operations for the scarlet dye; and, in general, the time is shortened in proportion to the delicacy of the shades. For the *bouillon* of rose, the cherry *reddening* may be used; and *its* reddening is composed of a small quantity of solution of tin, tartar, and very little cochineal. The colour may be deepened, by passing the cloth through hot water on its coming out of the bath.

Flesh colour is made in the sequel of a *reddening*, by throwing away a little of the bath, and refreshing it with cold water. It may likewise be made in the sequel of the violets, by adding a little solution of tin. The boiling must continue but a very short time.

Lastly, the *reddening* from which the scarlet cloth has been withdrawn may serve for the greys that are to have a vinous cast, by refreshing the bath, adding to it gall-nuts, and then a little sulphate of iron, or green vitriol.

It must be observed, that the weak and delicate shades, such as the pinks and the oranges, as well as the lilacs, mallows, cherries, roses, have more lustre and freshness when they are prepared in a single bath, than when they are subjected to both the *bouillon* and the *reddening*. On this account it is sufficient to introduce into this bath the necessary ingredients. The cloth, when merely moistened, and unimpregnated with mordant, becomes charged with the colouring particles less readily, but in a more evenly manner. There is also in this mode of operating a saving of time and fuel.

## CHAPTER V.

*Of the Crimson Dye.*

ALL the processes employed for obtaining the different shades of crimson, from the lightest to the deepest, may be referred to two. The desired crimson hue is given either to cloth already dyed scarlet, or the crimson is given at first.

Alum, the salts in general with earthy base, the fixed alkalies and the volatile, possess the property of changing the colour of scarlet into crimson, which is the natural colour of cochineal. The cloth dyed scarlet has only to be boiled, therefore, during about an hour, in a solution more or less charged with alum, according as a deeper or lighter crimson is wanted; but as the other salts with earthy base have the same property, and as common waters contain more or less of these salts, it happens that they rose to a greater or smaller degree the scarlet shades passed through them, especially when they are heated. The quantity of alum necessary to obtain the crimson varies according to the nature of the waters employed; and when they are well charged with these salts, they may even suffice without the addition of alum. When a piece of scarlet has any defects, it is set apart for crimson.

Hellot says that he has tried soap, soda, potash, and the *cendres gravelées* (crude potash); that all these substances produced the crimson wanted, but that they deadened it, or gave it less lustre than alum. Ammonia, on the contrary, produces a very good effect; but as it evaporated speedily, a considerable quantity of it had to be put into the bath, which increased the price of the dye. He therefore thought of putting into the bath, somewhat more than tepid, a little muriate of ammonia, or sal ammoniac, and an equal quantity of common potash. The cloth assumed immediately a very rosy and very brilliant colour. He even thinks, that by this means, which heightens the colour, the quantity of the cochineal may be somewhat diminished. Poerner, who gives this very process, prescribes the leaving the scarlet for 24 hours in the cold solution of the ammoniacal muriate and potash.



To dye crimson directly, a solution of 5 ounces of alum, and 3 ounces of tartar, with 2 ounces of cochineal, are made use of in the *bouillon* for every 2 pounds 3 ounces of cloth; but solution of tin is commonly added, although in smaller proportion than for scarlet. The processes that are pursued vary much, according to the depth of the shade desired, or as it is more or less removed from the colour of scarlet. Some persons make use of the muriate of soda for the *bouillon*.

Archil and potash are often employed to brown crimsons, and give them more lustre; but this showy lustre (*bloom*) soon vanishes.

The *bouillon* for the crimson is made sometimes in the sequel of the *reddening* bath of scarlet, by adding to it tartar and alum; and it is asserted, that even the *soupe au vin*, (literally, wine-soup colour,) of which both the *bouillon* and the *reddening* are made in the sequel of scarlet, has more lustre than when it is formed from a fresh bath. For these colours, the wild cochineal may be substituted for the fine; but as it contains fewer colouring particles, its quantity must be augmented.

The *reddening* which has served for crimson may be employed for purples, and other compound colours, of which we shall treat hereafter.

Half scarlets and half crimsons, (half grain scarlets,) are made by replacing the half of the cochineal with madder, giving, moreover, the same *bouillon* as for scarlet, and following, as to the rest, the process of the *reddening* of scarlet or crimson. Instead of a half, other proportions of madder may be employed, according to the effect wanted. More lustre is also given to the ordinary madder red, by forming its *bouillon* in the sequel of the *reddening* of scarlet.

On silk, the fine crimson due to cochineal is distinguished from the false crimson obtained from brazil wood.

Silks intended to be dyed cochineal crimson, should be boiled only at the rate of 20 parts of soap for 100 of silk, because the slightest yellow cast which remains on the silk, when it is scoured only to this degree, is favourable to this colour.

Silks well cleansed in the river, are put into an aluming of the greatest possible strength; there they are usually left from the evening till next morning, after which they are washed and subjected to two beetlings in the river.

For preparing the bath, an oblong boiler is filled with water, to about one-half or two-thirds; and when this water boils, pounded white nut-galls are thrown in to about a 6th or an 8th of the weight of the silk; and after boiling a few seconds, there is put into the bath bruised and sifted cochineal, from an eighth to a fifth for each quantity of silk, according to the shade that is wanted. To the bath is afterwards added a sixteenth of tartar for one part of cochineal, and, when the tartar is dissolved, as much solution of tin. This solution should contain much more tin than that made use of for scarlet, otherwise the colour would be too bright. Macquer directs it to be made with sixteen parts of nitric acid, two of ammoniacal muriate, as much fine grain tin, and twelve of water.

The ingredients are mingled, and the boiler is filled up with cold water; the proportion of the bath being about 4 or 4½ gallons of water for every 2 pounds three ounces of silk. The silks are immediately plunged, turning them round the skein sticks till they appear very uniform. The fire is then increased, and the bath is kept boiling for two hours, turning round the silks from time to time; after which the fire is withdrawn, and the silks are plunged into the bath. Here they are kept for some hours. They are then washed in the river, giving them two beetlings, when they are wrung and dried.

If it be wished to brown the crimsons, they are passed, after washing them, through a solution more or less charged with sulphate of iron, according to the shade wanted. If the silk is to retain a shade of yellow, more or less of the decoction of the fustet wood is added to this solution.

White gall-nuts are preferable, because black ones deaden the colour of crimson; and if even too large a quantity of the former be introduced, the colour becomes duller. Macquer says that the galls serve merely to increase the weight of the silk; their general effect, however, is to render the colours more durable. They are indispensable, at least for the crimsons intended to be browned, (saddened.)

The test of vinegar, often used for distinguishing the cochineal crimson from the spurious, is deceitful, because it cannot distinguish the colours obtained from (brazil) wood, when they are fixed by means of the solution of tin; for in this case they resist the vinegar as well as those made with cochineal.

Macquer gives the description of the crimson silk dye of Damascus and Diarbekir, which was communicated by Granger; as also of the process followed at Genoa.

We have seen that a very small quantity of solution of tin was put into the bath for dyeing silk crimson. Were it wished to employ the same process by which wool is dyed scarlet, the silk would lose its lustre, (bloom,) and acquire but a faint colour; but Macquer and Scheffer have both published a process, differing only in some circumstances, for dyeing silk rose and *ponceau*, (deep red,) by means of solution of tin, employed cold, in order to avoid its too lively action on the silk.

In the process which Macquer published in 1768, the solution of tin is prepared by throwing three parts of tin very gradually into a mixture of four parts of nitric acid, and two of muriatic. When the solution is finished, six parts of silk are introduced, which has had previously a bath of annotto; there it is left for half-an-hour, when it is wrung out and washed, till the water ceases to be foul. For dyeing one pound of silk, 1-4th of cochineal, with 1-16th of tartar is employed. The liquor is made to boil; it is diluted with cold water, so that the hand can bear its heat: into this the silk is immersed, the fire is raised, and after a minute's ebullition it is taken out and washed. The silk receives, by this process, an augmentation of weight amounting to a fourth; its colour resists soap, and is much more durable than that given by carthamus, (safflower.)

In 1751, Scheffer published in Swedish the following process. One part of tin is dissolved in four parts of nitric acid, and one of muriate of soda; and the solution is diluted with a double quantity of water. In this the silk is left to macerate for 24 hours; when it is taken out and washed in clear water till this is no longer milky. The silk is then dyed, by boiling it for a quarter-of-an-hour with 5-6ths of its weight of cochineal, in a bath not much diluted: the remaining liquor contains still a good deal of colouring matter, which may serve to dye silk of a lighter shade, or indeed to dye it crimson by the ordinary process; it may serve likewise for wool.

Scheffer describes some variations of his process for obtaining different shades, of which we shall now recapitulate the principal. On wringing silk out of the solution of tin, letting it lie all night in a cold solution of one part of alum to thirty-two of

water, wringing it in order that it may be dried, washing it, and then passing it through a bath of cochineal, it takes merely a pale poppy-red colour. If after diluting one part of solution of tin with eight parts of water, the silk be set to macerate in it for 12 hours; be afterwards kept all the night in the solution of alum; be then washed, dried, and passed through two baths of cochineal as above, adding to the second bath a little sulphuric acid, a beautiful poppy-red will be obtained.

The chief difference between the processes of Macquer and Scheffer, consists in the yellow ground which Macquer gives the silk. Scheffer employs a larger proportion of cochineal in the dyeing bath; but, from the report of the very persons who co-operated at Macquer's experiments in the manufactory of the Gobelins, it must be acknowledged, that the silk dyed by his process had never reached the scarlet hue. This colour, so much desired, has, however, induced dyers to multiply their attempts. Those who appear to have approached nearest to their object, begin by dyeing the silk crimson; they then cover this dye with that of carthamus, by the process hereafter described; and they give it finally a yellow dye in the cold. Thereby a beautiful colour is obtained. But the carthamus dye is destroyed by the action of the air, and the colour grows pretty speedily brown.

Cochineal is little used for dyeing cotton and linen, because a beautiful and permanent red can be given them by means of madder. Scheffer, however, describes a process which may be tried. The linen or cotton is steeped for 24 hours in a cold solution of tin; after which it is wrung, washed, and made to boil for a quarter-of-an-hour with 4-6ths its weight of cochineal. The cotton takes a light red. These colours bear the action of the sun, but not of soap. Berkenhout also gave, in England, a process, which, by Bancroft's description, differs little from that which we have given for silk; but it is said to produce merely a crimson, because there is no yellow in it.

The difference between the processes to which recourse must be had for giving silk and cotton the colour of scarlet, appears to depend on these substances having a much smaller disposition to unite with the colouring matter of cochineal, or with the combination of this colouring matter and tin; whence it results, that this combination separates, reunites in two considerable

masses, and precipitates before its union can be effected with the stuff. But this inconvenience is obviated by first impregnating the stuff with solution of tin, because the oxyde of tin, being combined with it, the colouring molecules of the cochineal come and fix themselves in it, in which case this compound can no more be precipitated. It therefore appears to us, that, in order to succeed in this process, our views must be directed towards the fittest means for producing, at first, a combination of the oxyde of tin with the stuff, without altering the latter; and then to give it a due alloy of the red of cochineal, and of yellow, either by the means of tartar, or by the admixture of a yellow colour.

## CHAPTER VI.

### *Of Kermes.*

THE kermes, (*coccus ilicis*, Linn.,) is an insect, found in several parts of Asia and the South of Europe. It was known to the ancients by the name of *coccum squarlatinum*, *coccus basiscus*, *infectorius*, *granum tinctorium*. That collected in Galatia and Armenia was preferred; at the present day it is gathered chiefly in Languedoc, Spain, and Portugal.

The kermes lives on a small oak, (*quercus coccifera*, Linn.) The females grow big, (*massives*,) and finally remain motionless, when they have nearly the form and size of a pea, and are of a reddish-brown colour. Their shape caused them to be long mistaken for the seeds of the tree on which they live; whence they were called grains of kermes. They have been also called vermillion..

The first person who spoke of them with tolerable accuracy, was Pierre de Quiqueran, bishop of Sénez, in 1550, *de laudibus provinciarum*.

The history of this insect is found in a memoir of Nissolle, "Acad. des sciences," 1714; and particularly in Reaumur's "Mémoires pour servir à l'histoire des insectes," tom. iv.

It is thought that the kermes takes its name from an Arabic

word, which signifies a little worm, *vermiculus*, from which comes the name vermilion also given it. Astruc derives the term from two Celtic words, of which one signifies oak, and the other acorn. "Mémoire pour servir à l'histoire naturelle de Languedoc."

The kermes is fixed to the bark of the shrub by a white cottony down, furnished by the insect. Chaptal has observed that this down, as well as that which all the insects of this kind afford, has several of the characters of caoutchouc; that it was insoluble in alcohol, that it melted at the heat of boiling water, and burned with flame on red-hot cinders. To him we owe the following description of the method pursued at Languedoc to make the harvest of kermes.

"Towards the middle of the month of May, they begin to gather the kermes, which has then acquired its ordinary size; it resembles in its colour and form a little sloe. This harvest usually lasts till the middle of the month of June, and sometimes longer, if the great heats be retarded, or if violent rains do not come on; for one storm of rain is sufficient to put an end to the crop for a year. Women are commonly employed in this harvest. They go out early in the morning with a lantern in their hands, and a glazed earthen pot, and thus proceed before day-break to detach the kermes from the branches with their fingers. This time is the most favourable; 1st. because the leaves which are furnished with prickles give them less annoyance, being softened by the morning dew; 2d, because the kermes weighs more, either from its not being dried by the sun, or from fewer young ones making their escape, which are hatched by the heat. Persons are, however, to be seen sufficiently intrepid to gather it during the day-time, but this is rare.

"One individual can gather from one to two pounds in a day.

"In the first season of the harvest, the kermes weighs more; hence it sells for less than towards the conclusion, when it is drier and lighter.

"The price of fresh kermes varies, moreover, according to the demand of purchasers and its scarceness. It commonly fetches from 15 to 20 sous (halfpennies) per pound at the commencement, and from 30 to 40 towards the conclusion of the harvest.

"Those who purchase it are obliged as soon as possible to put

a stop to the development of the eggs, so as to prevent the escape of the young contained in the *coque*. This *coque* (shell) is merely the body of the mother, which has enlarged by the formation of the eggs. The female has no wings. It fixes and takes up its abode on a leaf. The male comes to impregnate her, and she then enlarges merely by the development of the eggs. In order to kill the young contained in the eggs, the kermes is steeped in vinegar for 10 or 12 hours, or it is exposed to the fumes of vinegar, which takes less time, for half an hour is enough. It is then dried on cloths. This operation gives it a wine-red colour."

When the living insect is crushed it affords a red colour. It has a pretty agreeable smell, and a taste somewhat bitter, harsh, and pungent; when dry it communicates the same odour and taste to water and alcohol, which thereby acquire a deep red colour. The extract procured from its infusion retains this colour. (NOTE MM.)

To dye spun worsted with kermes, it is first boiled in water along with bran for half an hour; next for two hours in a fresh bath, with a fifth of its weight of Roman alum, and a tenth of tartar. *Sour* water is usually added to it. It is taken out after this ebullition and enclosed in a bag, which is carried to a cool place, and left there for some days. To form a saturated colour, there is put into a tepid bath three-fourths of kermes, or even a weight equal to that of the wool introduced into the bath at the first *bouillon*. As the density of cloth is more considerable than of spun worsted or wool in the fleece, it requires a fourth less salts in the *bouillon*, and of *kermes* in the bath. With smaller proportions of kermes, lighter and paler colours are obtained. When a series of shades is to be made, it is necessary to begin, as usual, with the deepest.

Hellot directs us to throw into the boiler containing the kermes a small handful of the refuse wool, (or cot,) before immersing what is to be dyed in it, and to let it boil there for an instant. It removes a species of black fecula, and the wool dipped afterwards assumes a finer colour.

Before carrying the newly dyed wool to the river, it may be passed through a water bath slightly tepid, in which a small quantity of soap has been dissolved. The colour thus takes some lustre, but it is a little rosed, that is to say, it gets a cast bordering on crimson.

By employing kermes with tartar, without alum, and as much solution of tin as for cochineal scarlet, Hellot has procured from a single bath an extremely lively cinnamon. The cloth having been macerated in a solution of sulphate of potash, it took with the kermes an agate-grey colour of considerable beauty and solidity; after maceration with sulphate of soda, a dirty grey of little permanence; with sulphate of iron and tartar, a fine grey; with tartar and sulphate of copper, an olive colour, and the same with nitrate of copper. The solution of bismuth, poured drop by drop into the kermes bath, produced a violet. All the acids turn it into a cinnamon bordering more or less on red, according as the acids are weaker, or in smaller quantity. The alkalis rose the colour, and render it dull.

The red colour which kermes communicates to wool, has much less lustre than the scarlet made with cochineal, which came to be preferred as soon as the art of heightening the peculiar colour of cochineal by means of the solution of tin became known; but the former has much more permanence, and spots of grease can be effaced from it without its colour being affected. It is the blood-red, preserved without alteration in the old tapestries. To the scarlet of kermes, the name of *grain scarlet* was given, because this insect was mistaken for a seed, (*graine*.) They gave it likewise the name of *scarlet of Venice*, because its principal manufactory was in that city.

The solution of tin was not omitted to be employed for kermes, as well as for cochineal; and Scheffer describes several processes for dyeing by this method with kermes; but its colour then verges on yellow or cinnamon, because the combination formed with the colouring matter and oxyde of tin retains from the impression of the acid a yellow colour, as happens to the colouring matter of madder.

The durability of the colour of kermes has often excited a regret that our dyers should have abandoned its use, for they employ very little of it at present. Some mixed a small quantity of it with the cochineal. It is observed, that this mixture contributed to give body to the colour, but it dimmed its lustre. The greater part of the kermes comes from the Levant.

Only a dull reddish colour has been hitherto given to silk, by means of kermes.

The scarlet, for which one-half of kermes and one-half madder



are employed, is called *half grain*. This mixture gives a very permanent colour, but not lively, bordering a little on blood colour. It is said that the turbans fabricated for the Levant, are dyed in this way at Orleans. A little brazil wood is probably added.

The *coccus polonicus* is a small round insect, found adhering to the roots of a species of *polygonum*, (*sclerantus perennis*.) It is collected towards the end of June, in some provinces of Poland. It appears to have properties similar to those of the kermes; but no use is made of it in Europe. It is sold to the Turkish and Armenian merchants. It is used in Turkey for dyeing wool, silk, and horse-hair; and women employ it for dyeing their nails.

There are several other insects which might equally afford a red colour; some even have been employed; but the advantages presented by cochineal have made their use be abandoned or neglected.

## CHAPTER VII.

### *Of Lac, or Gum Lac.*

LAC is a substance of a more or less deep red colour, which is brought to us from India, under different forms. This substance is a production analogous to that of bee-hives, constructed by a species of *coccus*, which Kerr and Roxburgh have described.\* It lives, and forms cells, on different species of shrubs. Geoffroy, who has given some interesting observations concerning this substance,† regards it as a true wax, which owes its colour only to the embryos of insects that have formed *alveoli*; (little holes in it of a nearly round form;) hence the name of gum is improper.

Several species of lac are distinguished, the principal being,  
1. Stick lac, the production which the ants have constructed round small branches. This species is the richest in colour, though there is some of it in Madagascar nearly colourless.

2. Grain, or seed lac. It is less coloured than the preceding.

3. Lac in tables (shell lac). It is imported in small plates of

\* Philos. Trans. 1781, 1791.

† Mem. de l'académie. 1714.

variable size and transparency. It has usually a dirty colour, and is mixed with some wood and earth. It would seem that the Indians have already extracted the colouring matter from it. These two latter kinds are employed for sealing wax; colouring them with minium (or vermilion) for red wax; with lamp-black for black wax; with orpiment for the wax of an aventurine colour, &c. Geoffroy says, that the lac, separated from the small bodies that it contains, afforded him, on distillation, the same products as wax; and that the small bodies, which may be ground into a fine red powder, afforded him the products of animal substances. The colouring particles, which are owing to these small bodies, which he takes for chrysalids, dissolve in water and alcohol, giving these liquids a fine red colour. (NOTE NN.)

For dyeing, stick lac must be chosen of the deepest colour. It is freed from the twigs, and reduced to powder.

The colour obtained from lac has not the lustre of the scarlet made with cochineal, but it has the advantage of possessing more permanence. It may be used profitably by mixing a certain quantity of it with cochineal; and if too great a proportion be not taken, the scarlet is no less beautiful, and it is more durable.

In order to separate the portion soluble in water, and to estimate its proportion to the wax or resin, Hellot was accustomed to extract it by means of water and mucilage of comfrey, to throw down its colouring matter with alum, to collect and dry it. He obtained by this process a precipitate which formed one-fifth of the weight of the lac, and it was this precipitate which he used for dyeing. But this precipitate is a combination of the colouring particles with alumina, or the base of alum.

Lac may be employed in a simpler manner: the only precaution is to boil the cochineal and the solution of tin for the proper time; after which the bath is refreshed, and the lac in powder is introduced. It requires a very moderate heat, otherwise it dyes in an unevenly manner, and also a still more considerable quantity of the tin solution than cochineal. The cloth should be washed very hot on coming out of the boiler, because the resinous particles attached to it are difficult to separate when cold. Lac may be employed with success for the *soupe au vin* colour, by putting it in the *bouillon*; into which, in this case, no alum must enter, because it would precipitate the colouring

matter too rapidly. Cochineal is used in the *reddening* bath, and it is saddened in the ordinary way.

According to Hellot, fixed alkali, or lime water, changes the lively red produced by lac into a wine-lees colour; and sal-ammoniac affords cinnamon, or bright chestnut colours, according as there is more or less salt.

Geoffroy conjectures, that lac is used for dyeing red morocco leather in the Levant, after being subjected to suitable preparations. In fact, lac appears to be employed along with cochineal for this purpose at Diarbekir; and at Nicosie kermes is used. Quemiset says, that kermes, cochineal, or lac, may be employed indifferently.\*

An advantageous distinction of lac over kermes appears to be, its bearing the action of solution of tin, and experiencing its good effects, without having its colour changed to yellow; and we have seen, that it requires even a larger proportion of it than cochineal does.

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## CHAPTER VIII.

### *Of Archil.*

THE archil used in dyeing, is in the form of a violet-red paste. Two kinds of it are chiefly distinguished, the archil plant of the Canaries, and the ground archil, (*de terre*), or that of Auvergne, called also *pérelle*. The first is by far the most esteemed. It is prepared from a species of lichen (*lichen roccella*) which grows on rocks adjoining the sea, in the Canary and Cape de Verd Islands. The second species is prepared from a lichen (*lichen parellus*) which grows on the rocks of Auvergne.

Micheli, as quoted by Hellot, says, that the workmen who prepare the archil at Florence, reduce the plant to a fine powder, which they pass through a sieve; that they then sprinkle it gently with stale urine; that they stir the mixture once a day, adding to it each time a certain proportion of soda in powder, till the materials have assumed a columbine (dove) colour. The

\* L'Art d'appreter et de teindre toutes sortes de peaux.

substance is now put into a wooden cask, and urine is added to it, or lime water, or solution of gypsum, till its surface be covered, in which state it is preserved. In a description to be found in the work of Plictho, sal ammoniac, sal gem, and salt-petre are added to this preparation; but Hellot convinced himself by experiments, that lime and urine were the sole ingredients necessary; and that it was requisite to stir up the mixture frequently, adding at the same time new doses of lime and urine. It is proper to let the volatile alkali, which is formed, evaporate at the end of the process, in order that the archil may assume the odour of violets, which characterizes the well-prepared article. To preserve it long, however, it must be kept moistened with urine.

Kalm says, in an appendix to a Memoir of Linnæus, in the Stockholm Transactions for 1745, that in some parts of Sweden two lichens, which he describes, are used for dyeing red. In the same Transactions for 1744, there is said to be found, likewise in Sweden, a species of lichen, (*lichen foliaceus umbilicatus sub-tus lacunosus*, Linn. Flor. Suec.) which, being prepared with urine, dyes wool and silk of a beautiful and permanent red or violet.

There are several other species of moss and lichen which might be employed in dyeing, were they prepared like the archil. Hellot gives the following method for discovering if they possess this property. A little of the plant is to be put into a glass vessel; it is moistened with ammonia and lime water in equal parts; a little muriate of ammonia (sal ammoniac) is added; and the small vessel is corked. If the plant be of a nature to afford red, after three or four days, the small portion of liquid, which will run off on inclining the vessel, now opened, will be tinged of a crimson red, and the plant itself will have assumed this colour. If the liquor or the plant does not take this colour, nothing need be hoped for; and it is useless to attempt its preparation on the great scale. Lewis says, however, that he has tested in this way a great many mosses, and that most of them afforded him a yellow or reddish-brown colour; but that he obtained from only a small number a liquor of a deep red, which communicated to cloth merely a yellowish-red\* colour.

\* The Chemical Works of Gaspard Neuman.

Prepared archil gives out its colour very readily to water, ammonia, and alcohol. Its solution in alcohol is used for filling spirit of wine thermometers; and when these thermometers are well freed from air, the liquor loses its colour in some years, as Abbe Nollet observed.\* The contact of air restores the colour, which is destroyed anew *in vacuo* in process of time. The watery infusion loses its colour by the privation of air in a few days; a singular phenomenon, which merits new researches.

The infusion of archil is of a crimson bordering on violet. As it contains ammonia, which has already modified its natural colour, the fixed alkalies can produce little change on it, only deepening the colour a little, and making it more violet. Alum forms in it a precipitate of a brown-red; and the supernatant liquid retains a yellowish-red colour. The solution of tin affords a reddish precipitate, which falls down slowly; the supernatant liquid retains a feeble red colour. The other metallic salts produce precipitates that offer nothing remarkable.

The watery solution of archil applied to cold marble penetrates it, communicating a beautiful violet colour, or a blue bordering on purple, which resists the air much longer than the archil colours applied to other substances. Dufay says, that he has seen marble tinged with this colour, preserve it without alteration at the end of two years.

To dye with archil, the quantity of this substance deemed necessary, according to the quantity of wool or stuff to be dyed, and according to the shade to which they are to be brought, is diffused in a bath of water as soon as it begins to grow warm. The bath is then heated till it be ready to boil, and the wool or stuff is passed through it without any other preparation, except keeping that longest in, which is to have the deepest shade. A fine gridelin, bordering on violet, is thereby obtained; but this colour has no permanence. Hence archil is rarely employed with any other view than to modify, heighten, and give lustre to the other colours. Hellot says, that having employed archil on wool boiled with tartar and alum, the colour resisted the air no more than what had received no preparation. But he obtained from herb archil (*l'orseille d'herbe*) a much more durable colour, by putting in the bath some solution of tin. The archil thereby

\* Mem. de l'acad. 1742.

loses its natural colour, and assumes one approaching more or less to scarlet, according to the quantity of solution of tin employed. This process must be executed in nearly the same manner as that of scarlet, except that the dyeing may be performed in a single bath.

Archil is frequently had recourse to for varying the different shades and giving them lustre: hence it is used for violets, lilacs, mallows, and rosemary flowers. To obtain a deeper tone, as for the deep *soupes en rin*, sometimes a little alkali or milk of lime is mixed with it. The sequel of this browning may also afford agates, rosemary flowers, and other delicate colours, which cannot be obtained so beautiful by other processes. Alum cannot be substituted for this purpose; it not only does not give this lustre, but it degrades the deep colours.

The herb-archil is preferable to the archil of Auvergne, from the greater bloom which it communicates to the colours, and from the larger quantity of colouring matter. It has, besides, the advantage of bearing ebullition. The latter, moreover, does not answer with alum, which destroys the colour; but the herb-archil has the inconvenience of dyeing in an irregular manner, unless attention be given to pass the cloth through hot water as soon as it comes out of the dye.

Archil alone is not used for dyeing silk, unless for lilacs; but silk is frequently passed through a bath of archil, either before dyeing it in other baths, or after it has been dyed, in order to modify different colours, or to give them lustre. Examples of this will be given in treating of the compound colours. It is sufficient here to point out how white silks are passed through the archil bath. The same process is performed with a bath more or less charged with this colour, for silks already dyed.

Archil, in a quantity proportioned to the colour desired, is to be boiled in a copper. The clear liquid is to be run off quite hot from the archil bath, leaving the sediment at the bottom, into a tub of proper size, in which the silks newly scoured with soap, are to be turned round on the skein sticks with much exactness, till they have attained the wished-for shade. After this, they must receive one beetling at the river.

Archil is in general a very useful ingredient in dyeing; but as it is rich in colour, and communicates an alluring bloom, dyers are often tempted to abuse it, and to exceed the proportions that

can add to the beauty, without, at the same time, injuring in a dangerous manner the permanence of the colours. Nevertheless, the colour obtained when solution of tin is employed, is less fugitive than without this addition. It is red, approaching to scarlet. It appears to be the only ingredient which can increase its durability. The solution of tin may be employed, not only in the dyeing bath, but for the preparation of the silk. In this case, by mixing the archil with other colouring substances, dyes may be obtained which have lustre with sufficient durability.

We have spoken of the colour of the archil, as if it were natural to it, but it is really due to an alkaline combination. The acids make it pass to red, either by saturating the alkali, or by substituting themselves for the alkali.

The lichen which produces archil is subjected to another preparation, to make turnsole (*litmus*.) This preparation is made in Holland. The lichen comes from the Canary Islands, and also from Sweden. It is reduced to a fine powder by means of a mill, and a certain proportion of potash is mixed with it. The mixture is watered with urine, and allowed to suffer a species of fermentation. When this has arrived at a certain degree, carbonate of lime in powder is added, to give consistence and weight to the paste, which is thereafter reduced into small parallelopipeds, that are carefully dried.\*

## CHAPTER IX.

### *Of Carthamus.*

CARTHAMUS or safflower (*carthamus tinctorius*), the flower of which alone is used in dyeing, is an annual plant cultivated in Spain, Egypt, and the Levant. There are two varieties of it, one which has large leaves, and the other smaller ones. It is the last which is cultivated in Egypt, where it forms a considerable article of commerce.

Formerly carthamus was cultivated in Thuringia and Alsace; but the preference given to that of the Levant has caused its

\* Journal des artes et manufactures, tom. ii.

culture to be almost entirely abandoned in our climates. The celebrated Beckman, who has given a very interesting dissertation on carthamus,\* has sought to discover the difference between that raised in our climate, and that imported from the Levant; but before availing ourselves of his observations, it is proper to describe the properties of this substance, such as it is employed in dyeing.

Carthamus contains two colouring matters, one yellow and the other red. The first, alone, is soluble in water; its solution is always turbid: with reagents, it exhibits the characters usually remarked in yellow colouring matters; the alkalis render it lighter, the acids deepen it, giving it more of an orange hue; both produce a small dun precipitate, in consequence of which it becomes clearer. Alum forms a precipitate of a deep yellow in small quantity. The solution of tin and the other metallic solutions cause precipitates, which have nothing in them remarkable.

Alcohol takes but a slight dye from these flowers, out of which all the yellow substance had been extracted by sufficient washings (with water). If such flowers be put into a solution of caustic alkali, they become yellow, and the liquor expressed from them is of a deep yellow. On saturating the alkali with an acid, the liquor becomes turbid, reddish, and deposits a reddish-yellow precipitate in small quantity. A yellow precipitate is formed, with solutions of alum, zinc, and tin; and a precipitate bordering on green, with solutions of iron and copper. If a carbonate of an alkali has been used, the acids produce an abundant and a redder precipitate; but the shade differs according to the acid employed. Alum produces also with the latter alkaline solution a red precipitate, which is so light that it usually floats on the surface of the liquor. This colouring matter is so delicate, so easily affected, that if heat be employed for dissolving it, the precipitates by the acids have no longer the same beautiful colour.

Beckman has observed, that the carthamus of Thuringia contains far more yellow matter than that of the Levant; that in other respects the red matter of the former did not yield in beauty to that obtained from the latter; but that in order to

\* Comment societ. Gotting. tom. iv. 1774.



obtain an equal effect, one-half more of the one was required than of the other. He inquired if this difference depended on climate, or only on the preparation.

Hasselquist relates, in his *Voyage d'Egypte*, that when the flowers of carthamus are gathered, they are squeezed between two stones to express their juice ; that they are thereafter washed several times with pit-well water, which in Egypt is naturally saltish ; that, on coming out of the water, they are pressed between the hands, and then spread out on mats upon terraces ; that they are covered during the day, to hinder the sun from drying them too much ; but that they are exposed to the dew during the night ; that they are turned over from time to time ; and that when they are found to be dried to the proper point, they are taken up, and preserved for the market, under the name of *saffranon* (safflower).

If the carthamus of the Levant, as found in commerce, be compared with that of Thuringia, the former is observed to be purer, a little damp, and in compressed masses ; while the latter is drier and more elastic. These differences depend on the preparation. The authors on agriculture, misled by the false denomination of bastard saffron, given to carthamus, have thought it should be treated like saffron. They consequently direct to gather it in a dry season, and also to dry it with much care. Beckman conceives that we should, on the contrary, imitate the method adopted in Egypt : he recommends to add even a little salt to the water used in the preparation, that it may have the same quality as in Egypt.

The flower of carthamus has a fine flame colour ; it should be gathered only when it begins to fade, and it is better when it has received rain in this state, although there be a prejudice to the contrary. The rain may be supplied by an artificial watering of the flowers morning and evening. The seeds may still be left to ripen after the blossom is cropped.

These directions are given with the view of separating the yellow substance, a redundance of which may constitute the difference between the carthamus of our climate and that of the Levant. It is proper to keep the carthamus in a moist place, for too strong desiccation might injure it.

Many motives should induce us to enrich our agriculture with this production. The seeds of carthamus serve as a very good

nourishment to poultry, but particularly to parrots, whence they have got the name of parrot seeds. A useful oil may be expressed from them, and the residue may be given to cattle. The dry leaves and twigs may serve as fodder to sheep and goats during winter; and the stronger stems, which the animals have stripped, may be used for fuel. Beckman has proved, that carthamus ripened well at Gottingen, where the soil is sandy. The ground should be dunged in moderation, and the plant must be neither watered nor transplanted. We have seen some of it grown at Amiens by the care of Lapostolle, which was of good quality.

The yellow matter of carthamus is not employed; but in order to extract this portion, the carthamus is put into a bag, which is trodden under water, till no more colour can be pressed out. The flowers, which were yellow, become reddish, and lose in this operation nearly one half of their weight. In this state they are used.

The yellow colouring substance might however be employed. Poenor has made several experiments on this subject. Their principal result is, that wool takes without preparation a yellow hue which is not durable, but that which it takes after alum and tartar is better, although it is not very permanent. Beckman says, that cloth prepared with tartar, or with tartar and alum, takes a good yellow colour, and that, in equal weight, carthamus contains more yellow colouring matter than yellow wood (old fustic) itself.

For extracting the red part of carthamus, and thereafter applying it to stuff, the property which alkalies possess of dissolving it is had recourse to, and it is afterwards precipitated by an acid. Beckman says, that next to citric acid (acid of lemons), sulphuric acid has the best effect, provided only the due proportion be employed; otherwise it alters and destroys the colour. According to Scheffer, we may substitute for lemon juice the juice of the berries of the mountain-ask (*sorbus aucupatorius*), which is to be thus prepared. These berries are to be beat in a mortar with a wooden pestle, and the juice is to be strained off, and allowed to ferment. It is then put into bottles; and the clear portion, which is sourest, is better fitted for this process the older it is. This preparation requires some months, and should be undertaken only in summer.

The process of dyeing consists, therefore, in extracting the red colouring matter by means of an alkali, and precipitating it on the stuff by means of an acid. It is this fecula which serves for making the rouge employed by ladies.

As to this rouge, the solution of carthamus is prepared with crystallized carbonate of soda, and it is precipitated by lemon juice. It has been remarked, that lemons beginning to spoil were fitter for this operation, than those that were less ripe, whose juice retained much mucilage. After squeezing out the lemon juice, it is left to settle for some days. The precipitate of carthamus is dried at a gentle heat, on plates of stone-ware; from which it is detached and very carefully ground with talc, which has been reduced to a very subtile powder, by means of the leaves of shave grass, (*presle*,) and successively passed through sieves of increasing fineness. It is the fineness of the talc, and the greater or less proportion which it bears to the carthamus precipitate, which constitute the difference between the high and low-priced *rouges*.

Wool may be dyed red by means of carthamus, as Beckman has ascertained. This dye passes, however, very readily to orange, and the power of obtaining from cochineal the finest and most varied reds, which are at the same time much more permanent than those of carthamus, makes the latter be rejected for wool.

Carthamus is used for dyeing silk, poppy, *nacarat*, (a bright orange-red,) cherry, rose colour, and flesh colour. The process differs, according to the intensity of the colour, and the greater or less tendency to flame colour that is wanted. But the carthamus bath, whose application may be varied, is prepared as follows.

The carthamus, from which the yellow matter has been extracted, and whose lumps have been broken down, is put into a trough. It is repeatedly sprinkled with *cendres gravelées* (crude pearl ashes,) or soda (barilla) well powdered and sifted, at the rate of  $6\frac{1}{2}$  pounds for 110 pounds of carthamus: but soda is preferred; mixing carefully as the alkali is introduced. This operation is called *amestrer*. The *amestred* carthamus is put into a small trough with a grated bottom, first lining this trough with a closely woven cloth. When it is about half filled, it is placed over the large trough, and cold water is poured into the

upper one, till the lower becomes full. The carthamus is then set over another trough, till the water comes from it almost colourless. A little more alkali is now mixed with it, and fresh water is passed through it. These operations are repeated till the carthamus be exhausted, when it turns yellow.

After distributing the silk in hanks on the rods, lemon juice, brought in casks from Provence, is poured into the bath, till it becomes of a fine cherry colour; this is called *turning* the bath, (*virer le bain.*) It is well stirred; and the silk is immersed, and turned round the skein sticks in the bath, as long as it is perceived to take up the colour. For *ponceau* (poppy colour) it is withdrawn, the liquor is wrung out of it on the peg, and it is turned through a new bath, where it is treated as in the first. After this it is dried and passed through fresh baths, continuing to wash and dry it between each operation, till it has acquired the depth of colour that is desired. When it has reached the proper point, a brightening is given it, by turning it round the sticks seven or eight times in a bath of hot water, to which about half a pint of lemon juice for each pailful of water has been added.

When silk is to be dyed poppy or flame colour, it must be previously boiled as for white; it must then receive a slight foundation of annatto, as will be explained in treating of this substance. The silk should not be alumed.

*Nacarats*, (orange-reds,) and deep cherry colours, are given precisely like the poppy-reds, only they receive no annatto ground; and baths may be employed which have served for the poppy-red, so as to complete their exhaustion. Fresh baths are not made for the latter colours, unless there be no occasion for the poppy.

With regard to the lighter cherry-reds, rose colours of all shades, and flesh colours, they are made with the second and last runnings of the carthamus, which are weaker. The deepest shades are passed through first.

The lightest of all these shades, which is an extremely delicate flesh colour, requires a little soap to be put into the bath. This soap lightens the colour, and prevents it from taking too speedily, and becoming unevenly. The silk is then washed, and a little brightening is given it, in a bath which has served for the deeper colours.

All these baths are employed the moment they are made, or

as speedily as possible, because they lose much of their colour on keeping, by which they are even entirely destroyed at the end of a certain time. They are, moreover, used cold, to prevent the colour from being injured. It must have been remarked, in the experiments just described, that the pure alkalies attack the extremely delicate colour of carthamus, making it pass to yellow. This is the reason why crystals of soda are preferred to the other alkaline matters. Those at least should be selected which contain most carbonic acid, as salt of tartar.

In order to diminish the expense of the carthamus, it is the practice, for the deeper shades, to mingle with the first and the second bath about 1-5th of the bath of archil. .

For dyeing on raw silks, such as are very white should be chosen, and be treated like boiled silks, with this single difference, that the poppies, the orange-reds, the cherries, should be commonly passed through the baths which have already served to make the same colours with boiled silk, because raw silk is, in general, more easily dyed than boiled.

The poppy having been prepared in an acid liquid, resists the proof by vinegar; but it is speedily altered and destroyed in the air. Scheffer says, that the colour for which mountain-ash berry juice has been used instead of lemon juice, resists for a longer period.

Beckman made experiments on the application of the red colour of the carthamus to cotton.\* He macerated cotton for two hours in melted hog's lard; he washed it well, and after this dyed it, in the ordinary way, with carthamus deprived of its yellow matter. This cotton took a deeper colour than that which had received no preparation. Soap succeeded equally well, olive oil still better. Beckman next passed cotton several times through oil, drying it alternately. After the last drying, he washed and dried it. He passed it through the yellow bath of carthamus, to which he added nut-galls and alum; and, lastly, he dyed it with the alkaline solution of carthamus and lemon juice. He thus obtained a beautiful and saturated red colour. The cotton treated without being impregnated with oil, took a colour of the same kind, but it was less saturated, and withstood

\* *Experimenta Lina xyliina tingendi flor. carth. tinct. commentationes*, Soc. Reg. Gotting. vol. iii. 1780.

less the action of the air. The author, from these experiments, imagines that it would be necessary to give cotton that is to be dyed with carthamus, preparations analogous to what it receives in the Adrianople red dye.

To dye cotton, poppy, Wilson directs us to put the carthamus well freed from its yellow colouring matter, into a vessel having a hair sieve near its bottom, and to pour over it a solution of pearl ashes, to mix well, and let the whole stand for a night. Next morning the liquid is drawn off by a stopcock at the bottom of the vessel. The piece of cotton to be dyed is plunged in, and turned through it by means of a winch. A solution of tartar is prepared, allowed to settle, and while it is still hot some of it is to be poured into the solution of carthamus till this liquid becomes a little sour. The cotton is to be perpetually turned about through this mixture, till it has assumed the wished-for shade. It is then to be slightly washed and dried in a stove. By this process it takes a very fine colour.

If it be desired to give a scarlet colour to cotton, it must first be dyed yellow by the process described in the chapter on annotto, and while still moist, it is to be dyed with carthamus, as above. It takes a colour as beautiful as scarlet, but one of little durability, which does not bear washing with water.

In Egypt, there is given to cotton, and even linen, a very saturated and somewhat permanent colour, by means of carthamus. The carthamus is subjected to two successive macerations, each of twenty-four hours, in pit-well water slightly alkaline. After this it is mixed with 1-5th of its weight of (alkaline) ashes, purchased from the Arabs, which contain a little carbonate of soda. This mixture is ground in a mill; and some water of the Nile is then filtered through it. By this means, a liquid strongly charged with colouring matter is obtained. They commence dyeing with the portion last filtered, which is feebly charged; they pour into it a little lemon juice; then mix in a boiler the first portion of the liquid, with a considerable quantity of lemon juice, and dye at a heat of 122°, or 145° Fahr. They finish, by passing the stuff through an acidulous water, and drying it.\*

\* Mémoires sur l'Egypte.

## CHAPTER X.

*Of Brazil Wood.*

THIS wood, which is much used in dyeing, derives its name from the part of America whence it was first imported. It has also the name of Fernambucca, wood of Saint Martha, or of Sapan, according to the places which produce it. At present it is cultivated in the Isle of France, where it has been naturalized. That of the Antilles, called *brésillet braziletto*, is least esteemed.

Linnaeus distinguishes the tree which furnishes the brazil wood, by the name of *cæsalpinia crista*; that of Japan, or the wood of Sapan, distinguished into large and little Sapan wood, by the name *cæsalpinia sapan*; and, lastly, he denominates the *brésillet*, *cæsalpinia vesicaria*.

This tree commonly grows in dry places, and amid rocks. Its trunk is very large, crooked, and full of knots. The flowers of the wood of Sapan, and the *brésillet*, have 10 stamina; those of the genuine brazil wood have only five. That which comes from Fernambucca is most valued.

Brazil wood is very hard, susceptible of a fine polish, and sinks in water. It is pale when newly cleft, but becomes red on exposure to air. It has different shades of red and orange. Its goodness is determined particularly by its density. When chewed, a saccharine taste is perceived. It may be distinguished from red saunders wood, as the latter does not yield its colour to water.

Boiling water extracts the whole colouring matter of brazil wood. If the ebullition be long enough continued, it assumes a fine red colour. The residuum appears black. In this case, an alkali may still extract much colouring matter. The solution in alcohol or ammonia is still deeper than the preceding. According to Dufay, a red colour, passing into violet, may be given by the alcohol of brazil wood to heated marble. If the heat be increased while the stained marbles are coated with wax, the colour runs through all the shades of brown, and settles into a chocolate.

The recent decoction of brazil wood affords, with sulphuric acid, a scanty red precipitate, bordering on dun; the liquor remains transparent, and of a yellow colour. Nitric acid makes the tincture pass at first to yellow; but if more of it be added, the liquor takes a deep orange-yellow colour, and becomes transparent, after depositing a precipitate nearly similar to the preceding, and more abundant. Muriatic acid comports itself like the sulphuric. Oxalic acid gives a precipitate of an orange-red, almost russet, and nearly as abundant as that of nitric acid. The liquor remains transparent, and of the same colour as the preceding. Distilled vinegar gives a very little precipitate of the same colour; the liquor remains transparent, and a little more of an orange hue. Tartar furnishes still less precipitate; the liquor remains turbid, and redder than the last. Fixed alkali brings down the decoction to crimson, or deep violet bordering on brown, and affords an almost imperceptible precipitate of the same colour. Ammonia gives a lighter violet or purple, and a fine purple precipitate in small quantity. Alum occasions a red precipitate verging on crimson, copious and slow of falling. The liquor floating over it retains a fine red colour, similar to that of the fresh decoction. This liquor affords, moreover, an abundant precipitate, if the acid of the alum be saturated with an alkali. Thus a species of carmine inferior to ordinary carmine, and a liquid lake for miniatures, may be prepared. Alum along with tartar forms a scanty brownish-red precipitate; the liquor remains very clear, and of an orange-red hue. The sulphate of iron causes the tincture to take a black colour bordering on violet; the precipitate is abundant, and of the same colour, as well as the supernatant liquor. The sulphate of copper gives, in like manner, abundance of precipitate, but it is much duller; the liquid remains transparent, and of a russet-brown. . Sulphate of zinc affords a scanty brown precipitate; the transparent liquor which stands over it is of the colour of pale beer. Solution of acetate of lead causes an abundant precipitate of a tolerably beautiful dark red; the transparent liquid is orange-red. The solution of tin in nitromuriatic acid affords a very abundant precipitate of a fine rose colour; the liquor remains transparent, and quite colourless. Lastly, with corrosive muriate of mercury a light precipitate,



of a brown colour, is obtained; the liquor remains transparent, and of a fine yellow hue.

In the *Journal de Physique*,\* very curious experiments are to be found on the action which the acids exercise on brazil wood. If, after having changed it to yellow by means of tartar and acetic acid, solution of nitro-muriate of tin be poured into it, there is immediately formed a very abundant rose precipitate. If to the solution made yellow by an acid, a larger quantity of this acid, or of a stronger acid, be added, the red colour is restored. Sulphuric acid is best adapted to produce this effect. Some salts, also, make the red colour of brazil reappear, after it has disappeared by the action of acids. (NOTE OO.)

The decoction of brazil wood, called juice of brazil, is observed to be less fit for dyeing when recent, than when old or even fermented. By age it takes a yellowish-red colour. For making this decoction, Hellot recommends to use the hardest water; but it should be remarked that this water deepens the colour in proportion to the earthy salts which it contains. After boiling this wood reduced to chips, or what is preferable, to powder, for three hours, this first decoction is poured into a cask. Fresh water is poured on the wood, which is then made to boil for three hours, and mixed with the former. When brazil wood is employed in a dyeing bath, it is proper to enclose it in a thin linen bag, as well as all the dye-woods in general.

Wool immersed in the juice of brazil takes but a feeble tint, which is speedily destroyed. It must receive some preparations.

The wool is to be boiled in a solution of alum, to which a fourth or even less of tartar is added, for a larger proportion of tartar would make the colour yellower. The wool is kept impregnated with it for at least eight days, in a cool place. After this, it is dyed in the brazil juice with a slight boiling. But the first colouring particles that are deposited afford a less beautiful colour; hence it is proper to pass a coarser stuff previously through the bath. In this manner a lively red is procured, which resists pretty well the action of the air.

If the red colour of brazil be destroyed by means of any acid

\* February, 1783.

whatsoever, it will give to woollen stuffs a fawn colour of greater or less depth, which is very durable in the air.

Poerner prepares the cloth with a *bouillon* composed of solution of tin, alum, and a little tartar; and he makes his bath with fernambucca, and a considerable proportion of alum. In the residuum of this bath he dyes a second piece, which has received a similar preparation. The first piece takes a fine brick colour, and the second a colour approaching to scarlet.\* The shades may be greatly varied by changing the proportions of the ingredients.

By these means sufficient permanence may be given to the colours derived from brazil wood; they cannot, however, be compared, in this respect, to those obtained from cochineal or madder. Bloom is sometimes given to the colour derived from the last substance, by passing the cloth dyed with it through juice of brazil; but this lustre soon goes off.

Guhliche gives a process by which he says that more beautiful and permanent colours may be obtained than by those now in use. He directs us to pour on the fernambucca, reduced to powder or in thin chips, pure vinegar, or aceto-citric acid,† or nitro-muriatic acid, till it be covered, and the liquor floats over it at a certain height; to agitate the mixture well, to let it settle for 24 hours, then to decant the liquor, filter, and preserve for use. A vegetable acid, or mere water, is poured upon the residuum. It is suffered to settle one or two days; it is filtered, and this practice is continued till the extraction of the colouring

\* Instruction sur l'art de la teinture.

† We call aceto-citric acid, an acid liquor of which Guhliche makes a great use in dyeing, under the name of vegetable acid spirit, and which he prepares in the following manner:—He takes lemons, such as have even the rind rotten may serve for this purpose; he separates the rind and adhering skin: he cuts them in slices, in a vessel which must not be of wood; he sprinkles them with a quantity of good vinegar, which he considers as approaching to that of lemons; he squeezes this mixture through flannel with a press, and filters the expressed juice through paper. In this state this liquor may be employed with success; but it has the inconvenience of growing mouldy, and the acid is very watery. He recommends us, in order to preserve it for use, and to have it in a more concentrated state, so that it may not dilute the baths into which it enters, to purify and concentrate it as follows:—The liquor is left exposed to the sun till it becomes clear, and till the deposit be formed. It is filtered and distilled on a sand bath. The receiver is to be changed when the drops become acid, and the distillation is continued till oily stræ be perceived on the neck of the retort. The acid found in the receiver is to be kept for use.

substance be completed. The wood is then black. The whole liquors are to be mixed together.

The stuff was first prepared by a feeble galling with sumach or white gall-nuts. After this a slight aluming is given. It is merely rinsed in water, and put quite moist into the bath, which is prepared as follows:—

The acid solution (infusion) of fernambucca is taken and diluted with a certain quantity of water, proportioned to the quantity of stuff, and to the force of the colour wished to be given. It is heated as high as the hand can bear. Solution of tin is now poured in, till the whole takes a flame colour; it is stirred, and the stuff is immersed and kept there for half an hour, when it is taken out and washed. The remainder of the bath may serve for the lighter shades. For these shades, the stuff should not be galled.

Brazil wood is made use of for dyeing silk what is called *false crimson*, to distinguish it from the crimson made by means of cochineal, which is much more permanent.

The silk should be boiled at the rate of 20 parts of soap per cent., and then alumed. The aluming need not be so strong as for the fine crimson. The silk is refreshed at the river, and passed through a bath more or less charged with brazil juice, according to the shade to be given. When water free from earthy salts is employed, the colour is too red to imitate crimson: this quality is given it by passing the silk through a slight alkaline solution, or by adding a little alkali to the bath. It might, indeed, be washed in a hard water till it had taken the desired shade.

To make deeper false crimsons of a dark red, juice of logwood is put into the brazil bath, after the silk has been impregnated with it. A little alkali may be added, according to the shade that is wanted.

To imitate poppy, or flame colour, an annotto ground is given to the silk, deeper even than when it is dyed with carthamus. It is washed, alumed, and dyed with juice of brazil, to which a little soap is usually added.

The solution of tin cannot be employed with brazil juice for dyeing of silk, in the same way as with cochineal, the reason of which is the same. The colouring particles separate too readily to be capable of fixing on the silk, which has not so efficacious

an attraction for them as wool has. But as Bergmann remarks, in his notes on the work of Scheffer,\* it is possible, by macerating the silk in a cold solution of tin, to improve greatly the colour of the dye-woods. A strong decoction of brazil, says he, gives to yellow silk a colour of scarlet, inferior, indeed, to that of cochineal, but more beautiful and more permanent than by the maceration of alum alone; and it can resist the proof by vinegar, like true crimson and poppy. Instead of employing raw silk, a yellow ground should be given to boiled silk, or a yellow substance may be mixed with the juice of brazil. Several dyers have been employed on this process more lately, and they have produced very diversified effects, by applying it to different colouring substances, which, of themselves, afford merely colours of little permanence, either by using them alone, or by forming different mixtures.

Poerner made a great many researches on the methods which may be employed to dye cotton by means of brazil, employing different mordants, as alum, solution of tin, sal ammoniac, potash, &c., in the bath, or in the preparation of the stuff; but he did not obtain colours which could resist the action of soap, although some of them stood pretty well the action of the air and washing with water. He recommends us to dry in the shade the cottons which have received these colours.†

To Brown, who is engaged with much zeal in the arts, we are indebted for a process which is used for a crimson on cotton in some manufactories.

A solution of tin is prepared in the following proportions: Nitric acid, four parts; muriatic acid, two parts; tin, one part; water, two parts. The liquids are to be mixed, and the tin dissolved in them, by adding it in small bits at a time.

For a piece of cotton velvet, weighing from 15 to 17½ pounds, we begin by preparing a bath composed of four parts of boiling water, and two parts of a strong decoction of nut-galls. The bath is raked up, the piece is let down into it, worked there for half an hour, and allowed to remain for two hours more; at the end of this time it is taken out, and set to drain. Another bath is prepared with three pailfuls of boiling water, and one pailful of decoction of wood of Fernambucca, also boiling. It

\* Essai sur l'art de la teinture.

† Versuche und bemerkungen zum nutzen der Farbekunst zweiter Theil.

is raked, and the piece is worked in it for an hour. This bath is emptied, and the vat washed out, and then filled with a clean boiling-hot decoction of wood. The piece is worked in this for half an hour, and lifted up on a winch. A bath of very clear river water is now got ready, into which nearly a quart of solution of tin is poured. After the bath is raked, the piece is worked in it for a quarter of an hour. It is then lifted on the winch, carried back above the vat containing the bath of decoction of fernambucca wood, one-sixth of which is taken out and replaced by an equal quantity of boiling solution. After raking up, the piece is worked in this bath for half an hour. It is raised upon the winch, and then transferred to the vat containing the solution of tin. This alternate working is repeated six or eight times, observing to withdraw each time one-sixth of the bath of fernambucca wood, and to replace it by an equal quantity of the boiling decoction of the same wood; to stir the bath of the composition every time with the rake; and to finish the dye by leaving it in the last bath. The piece is washed in a stream of water, and it is carefully dried in a dark place.

An analogous process is used for making the chocolates. After galling the cotton, it is alumed and maddered with an intermediate drying; it is next passed through the fernambucca, and the solution of tin. Some persons substitute muriate of tin for this solution.

In investigating the means best adapted to procure more permanence to the beautiful and varied colours that are obtained at little expense from brazil wood, it is proper to recapitulate some of its properties.

The colouring particles of brazil wood are easily affected, and made yellow by the action of acids. They thus become permanent colours. But what distinguishes them from madder and kermes, and approximates them to cochineal, is their re-appearing in their natural colour, when they are thrown down in a state of combination with alumina, or with oxyde of tin. These two combinations seem to be the fittest for rendering them durable. It is requisite, therefore, to inquire what circumstances are best calculated to promote the formation of these combinations, according to the nature of the stuff.

The astringent principle, likewise, seems to contribute to the

permanence of the colouring matter of brazil wood; but it deepens its hue, and can only be employed for light shades.

The colouring particles of brazil wood are very sensible to the action of alkalies, which give them a purple hue; and there are several processes in which the alkalies, either fixed or volatile, are used for forming violets and purples. But the colours obtained by these methods, which may be easily varied according to the purpose, are perishable, and possess but a transient bloom. The alkalies appear not to injure the colours derived from madder, but they accelerate the destruction of most other colours.

In England and Holland the dye-woods are reduced to powder by means of mills erected for the purpose. It appears, from the statement of Wilson, that they are kept moistened with urine, or, if this be not used, a little alkali is added when they are to be boiled.

The practice of reducing these woods to powder is of advantage, and ought to be generally adopted. In the Journal of Arts and Manufactures, (French,) volume first, is a description of the mills employed in Holland, and of the operations to which the dye-woods are subjected. When the woods are employed, and especially if they be in powder, it is proper to put them into a bag, before introducing them into the dyeing-baths. Putrefied urine and alkali, by promoting the extraction of the colouring particles, and increasing the tone of their colour, may frequently be hurtful to the effect wished to be obtained, or may accelerate their destruction. (NOTE PP.)

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## CHAPTER XI.

### *Of Logwood.*

LOGWOOD, (*bois d'Inde*,) wood of Campeachy, or of Jamaica, has received these different names from the places where it grows most plentifully. It is very common in Jamaica, and on the eastern shore of the Bay of Campeachy. It is found also at Santa Cruz, Martinique, and Grenada.

Linnæus calls the tree *hæmatoxylum campechianum*. It grows to a great height and thickness in a favourable soil. Its bark is thin, smooth, of a brilliant grey, and sometimes yellowish. Its trunk is straight, furnished with thorns: its leaves have some resemblance to those of the laurel, to which they also approach in their aromatic quality, whence the tree has got the name of the *aromatic* or *Indian* (bay) *laurel*. As its seeds have the taste of cloves, they have improperly got the name of *clove-seeds* (*graines de girofle*.) The English call them *Jamaica pepper*, or *all-spice*.

Logwood is so heavy as to sink in water. It is hard, compact, of a fine grain, capable of being polished, and scarcely susceptible of decay. Its predominant colour is red, with orange, yellow, and black tints.

For use, its juice is usually extracted like that of brazil wood. It yields its colour to both spirituous and watery menstrua. Alcohol extracts it more readily and abundantly than water. The colour of its tincture is a fine red, bordering a little on violet or purple, which is principally observable in its watery decoction. This left to itself becomes in time yellowish, and finally black. Acids change it to yellow, and the alkalies deepen its colour, bringing it to a purple or violet. Sulphuric, nitric, and muriatic acid occasion in it a slight precipitate, long in falling; which is of a dark red with sulphuric acid, a dead leaf (*feuille-morte*) colour with the nitric, and a lighter red colour with the muriatic. The supernatant liquor is transparent, of a deep red colour with the sulphuric and muriatic acids, and yellowish with the nitric. Oxalic acid forms a bright chestnut precipitate: the liquor remains transparent, of a yellowish red. Acetic acid comports itself in nearly the same way, only the colour of the precipitate is a little deeper. Tartar gives a precipitate like vinegar; but the liquor remains turbid, and inclines more to yellow. Fixed alkali forms no precipitate, but causes the solution to pass to deep violet, which eventually becomes almost brown. Alum occasions a pretty abundant precipitate, of a light violet hue: the liquor remains violet, and nearly transparent. Alum and tartar together produce a pretty copious red-brown precipitate, and of a yellowish red. Sulphate of iron gives immediately a blueish-black colour, like that of ink, a precipitate is formed of the same colour, and the liquor re-

mains long turbid; but if it be sufficiently diluted, and especially if there be a slight excess of sulphate, the whole black matter finally falls down. Sulphate of copper produces a very copious precipitate, of a browner and less brilliant black than the preceding. The liquid remains transparent, of a very deep yellowish or brownish red. Acetate of lead causes immediately a black precipitate, with a slight reddish tint. The liquid remains transparent, of a pale beer colour, and very bright. Lastly, tin dissolved in nitro-muriatic acid instantly forms a precipitate of a very fine violet colour, or purple, almost *prune de monsieur*. The supernatant liquor is very clear and totally colourless.

Stuffs would take in the decoction of logwood but a feeble and fugitive colour, were they not previously prepared with alum and tartar. A little alum is also added to the bath. By this means they take a pretty fine violet.

A blue colour may be obtained from logwood, by mingling verdigris with the bath, and passing the cloth through it till it has taken the desired shade.

These uses of logwood have obtained for it the names of *violet wood* and *blue wood*. When treating of the compound colours, these hues will be more fully considered.

The main employment of logwood is for blacks, to which it gives lustre and velviness; and for greys of certain shades. It is very extensively used also for different compound colours, which it would be difficult to obtain as beautiful and as diversified by the ingredients of a more permanent dye.

The juice of logwood is often mixed with that of brazil wood, to render the colours of a variable depth, according to the proportions in which this mixture is made.

Logwood is used for dyeing silk violet, prior to which the silk must be scoured, alumed, and washed, because without aluming it would take only a reddish tint, which would not bear wetting. This dye must be performed by turning the silks cold round their skein sticks, in the decoction of logwood, till they have acquired the colour that is wanted, because with heat there is obtained merely a speckled and uneven colour.

Bergmann long ago remarked, that a more beautiful and permanent violet might be formed from logwood, by impregnating the silk with a solution of tin, as has been stated in the pre-



ceding chapter. There is thus obtained, indeed, especially by mixing the logwood with brazil wood in different proportions, a great many beautiful shades, bordering more or less on red, from lilac to violet.

If decoction of logwood be employed for that of brazil wood in the process communicated by Brown, a fine violet colour is obtained; and if the two decoctions be mixed together, shades of puce and *prune de monsieur* will be got, inclining more or less to red.

The observations which have been given on brazil wood are applicable to logwood, whose colouring matter presents analogous properties. We shall only add, that in order to determine the differences resulting from the state of oxydation of the tin, when its solutions are used, we precipitated a decoction of fernambucca, and a decoction of logwood, with the proto-muriate of tin, and with the highly oxydized muriate. The lakes thrown down by the former had at first less lustre; but on exposure to air they soon acquired the same tone as those proceeding from a highly oxydized salt. We have, in like manner, impregnated silk with the solution of the same salts, and then dyed them with brazil wood and with logwood, when the superiority of colour was in favour of the patterns which had received the least oxydized salt.

When logwood has been employed in a process without solution of tin, it may be recognized by the red colour which the dyed stuff receives from an acid. (NOTE QQ.)

## SECTION IV.

### OF YELLOW.

## CHAPTER I.

### *Of Weld.*

WELD, or woald (*la goude* or *vaude*, in French, *reseda luteola*, Linn.), is a very common plant in the neighbourhood of Paris, in the greater number of our departments, and a great portion of the rest of Europe.

This plant puts forth long narrow leaves of a lively green. From the midst of these leaves the stem rises to about the height of a yard. It is often branchy, furnished with narrow leaves like the radical ones, but shorter as they approach the flowers, which are disposed in long spikes. The whole plant, except the root, serves for dyeing yellow.

Two kinds of weld are distinguished,—the wild or bastard weld, which grows naturally in the fields,—and the cultivated weld, which pushes forth stems of less height and thickness. The latter is preferred for dyeing; it abounds much more in colouring matter. It is esteemed in proportion to the slenderness of the stalks.

When the weld is ripe it is plucked up, allowed to dry, and put up in bundles. In this state it is employed.

When the decoction of weld is highly charged, it has a yellow colour bordering on brown; when much diluted with water, its yellow is more or less pale, and inclines a little to green.

If a little alkali be added to this decoction, its colour deepens, and there takes place after a certain time a slight ash-coloured precipitate insoluble in the alkalies.

The acids in general render its colour paler, and occasion a small precipitate, which alkalies dissolve, with the assumption of a yellow colour verging on brown.

Alum forms with it a yellowish precipitate: the supernatant liquid retains a fine lemon colour. If a solution of alkali be

poured into this liquid, a precipitate forms of a whiteish-yellow, soluble in alkalies, but the liquid remains always coloured.

The solution of muriate of soda, and that of muriate of ammonia, make the liquor turbid, and at first of a somewhat deeper hue. By degrees a precipitate falls of a deep yellow, and the supernatant liquid retains a pale yellow colour, inclining a little to green.

The solution of tin produces an abundant precipitate of a bright yellow; the liquor continues long turbid, but little coloured.

Sulphate of iron produces a copious grey-black precipitate; the supernatant liquid retains a brownish colour.

Sulphate of copper causes a brownish-green precipitate; the liquor preserves a pale green colour.

The yellow colour which weld communicates to wool has little permanence, if the wool has not been previously prepared with some mordants. Alum and tartar are employed; and by this means the plant affords the purest yellow,—a colour which possesses the advantage of being durable.

For the *bouillon*, which is performed in the usual manner, Hellot prescribes four parts of alum for sixteen of wool, and only one of tartar. Several dyers, however, employ half as much tartar as alum. The tartar renders the colour lighter, but more lively.

For the *welding* (*gaudage*), that is to say, dyeing with weld, the plant, enclosed in a thin bag, is boiled in a fresh bath, which is loaded with a heavy wooden cross, that it may not rise to the surface of the bath. Some dyers let it boil till it falls to the bottom of the copper, after which they lay on it a *champagne* (a weight to keep it down.) Others rake it out when it is boiled, and throw it away.

Hellot prescribes from five to six parts of weld for one part of cloth; but so considerable a quantity is seldom employed, dyers contenting themselves with three or four parts, or even much less. • It is true that several dyers add to the weld a little quick lime and ashes, which favour the extraction of the colouring matter, and heighten its colour, but render it at the same time liable to change by the action of acids. The quantity of weld, however, should be proportioned to the depth of shade wanted.

It is possible to dye in the sequel of the first dippings, in order to obtain progressively paler shades, by adding water at each dipping (*mise*,) and keeping the bath boiling; but the light shades obtained by this means have not so much vivacity as when fresh baths are used, proportioning the quantity of weld to the shade desired.

If muriate of soda be added to the weld bath, its colour becomes richer and deeper. • Sulphate of lime or gypsum renders it also deeper; but alum makes it lighter and brighter, and tartar paler. Sulphate of iron, or vitriol, causes it to draw towards brown. The hues obtained from weld may be modified by similar additions, by the proportions of the weld, by the duration of the operation, and by the mordants employed for the preparation of the stuff. Thus Scheffer says, that by boiling the wool for two hours with one-fourth of solution of tin, and one-fourth of tartar, washing it, and boiling it 15 minutes with an equal quantity of weld, it takes a beautiful colour, but one which does not penetrate into the interior. Poerner directs us also to prepare the cloth as for the scarlet dye. By this means, more lustre and permanence are given to the colour, which, *cæteris paribus*, is also brighter.

The colour may be farther modified by passing the cloth, on its coming out of the dye, through another bath. Thus, to make a golden yellow, the cloth, on its leaving the welding, is to be turned through a slight bath of madder; and to give it a tan colour, it is to be passed through a bath made with a little soot. These methods will be spoken of in treating of saddenings (*brunitures*).

To dye silk of a plain yellow (*jaune franc*,) no other ingredient is commonly used except weld. The silk must be scoured at the rate of 20 pounds of soap to the 100; afterwards alumed and refreshed, that is to say, washed after the aluming.

A bath is made with two parts of weld for one of silk, and after a full quarter of an hour's ebullition; it is filtered through a sieve, or cloth, into a vat. When this bath is sufficiently cooled to allow the hand to be plunged into it, the silk is immersed and turned round the sticks till it be uniform. During this operation, the weld is boiled a second time in fresh water. About one half of the first bath is thrown out, and it is replaced by the second *bouillon*. This fresh bath may be

employed a little hotter than the first; too great a heat, however, must be avoided, by which a portion of the colour already attached would be dissolved. It is to be turned as before, and meanwhile, some crude pearl ash is to be dissolved in a portion of the second *bouillon*. The silk is to be taken out of the bath, in order to add to it more or less of this solution, according to the shade that is wanted. After some turnings, a hank is wrung with the pin, to see if the colour be sufficiently full and golden. If it be not enough so, a little more of the alkaline solution is added, the property of which is to deepen the colour, and give a golden hue. The process is continued, as before, till the silk has attained to the wished-for shade. The alkaline solution may be added also, at the same time, with the second *bouillon* of weld, always taking care that the bath be not too hot.

If more golden-yellows be wanted, bordering on jonquille, it is necessary, when the ashes are put into the bath, to add some annatto, in proportion to the shade desired.

For the light yellow shades, as pale lemon and canary, the silk must be scoured as for blue, because these shades are more beautiful and transparent the whiter the ground is on which they are placed. The strength of the bath is proportioned to the shade sought for. If the yellow be wished to have a cast verging on green, more or less of the (indigo) vat is added, if the silk has been scoured without azure. To prevent these shades from being too deep, a slighter aluming than usual may be given to the silk.

Scheffer directs us to soak the silk for 24 hours in a solution of tin, prepared with four parts of nitric acid, one of muriate of soda, and one of tin, the solution being saturated with tartar; to wash it, and boil it for half an hour with its own weight of flowers of weld. He says that a fine straw colour is thereby obtained, which has the advantage of resisting the acids. In adopting this process, very little tin must remain in the solution, because the tartaric acid throws it down. The observations which we have previously made on the use of tin, may be applied here.

For dyeing cotton yellow, the first thing is to scour it in a bath prepared with a lixivium of the ashes of green wood, then to wash and dry it. It is alumed with the fourth of its weight of alum. After twenty-four hours it is taken out of the alum-

ing and dried, without washing. A weld bath is thereafter prepared, at the rate of one part and a quarter of weld for one of cotton. In this the cotton is dyed, by turning it round the sticks, and working it with the hands, till it has acquired the wished-for shade. It is taken out of this bath to be macerated for an hour and a half in a solution of sulphate of copper or blue vitriol, in the proportion of one-fourth of this salt to one part of cotton. It is next thrown, without washing it, into a boiling solution of white soap, made in the same proportions. After being well stirred, it is to be boiled for nearly an hour, after which it must be well washed and dried.

If a deeper yellow, bordering on jonquille, be wanted, the cotton is not passed through the aluming, but two parts and a half of weld are employed to one of cotton, with the addition of a little verdigris dissolved in a portion of the bath. The cotton is plunged into it, and worked, till it has taken an uniform colour. It is lifted out of the bath that a little soda ley may be poured in, when it is again immersed and turned through the bath for a full quarter of an hour. It is then withdrawn, wrung, and dried.

Lemon yellow is made by the same process, except that only one part of weld is used (for one of cotton,) while the quantity of verdigris can be diminished in proportion, or even entirely omitted, and aluming put in its place. Thus the shades of yellow may be varied in many ways. The operations on linen yarn are the same.

For the yellow colours on printed cotton goods, these are impregnated, by means of engraved plates, with the mordant described in treating of madder, formed by the mixture of acetate of lead and alum: the yellow colour induced on the parts not impregnated with the acetate of alumina, is to be afterwards destroyed by the action of bran, and exposure on the grass. The same mordant may be successfully employed for cotton and linen which is to be dyed yellow.

In order to obtain from weld the whole colour that it can yield, it must be boiled for three quarters of an hour; the bundles of weld are now taken out of the bath, after which the cloths are passed through it, at a temperature a little below ebullition. They should not remain in it more than twenty minutes.

When the same piece of cloth is to exhibit the colours produced by both madder and weld, it is necessary to begin with the madding, and not to print on the mordant intended for the weld till the operations of the madder are finished. This rule is founded on the property which madder possesses of fixing itself in the room of the yellow of weld; so that if the madding be long continued after dyeing with weld, the colour of the latter entirely disappears. Weld, on the contrary, does not affect the colour produced by madder, provided the mordant has been saturated with the latter, for otherwise a mixed colour would be produced.

The operations required for restoring the white are much longer, and demand much nicer management, after welding than after madding.

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## CHAPTER II.

### *Of Fustic (Bois Jaune.)*

THIS is the wood of a large tree (*morus tinctoria*), which grows in the Antilles, and principally at Tobago. It is of a yellow colour, as its name denotes, and it has orange veins. Its medullary prolongations are very thin. It is neither very hard nor heavy.

The use of this wood for dyeing has only become general of late years. It abounds much in colouring matter, affording a colour which is permanent, especially on woollen stuffs. It unites well with indigo; has a moderate price; and its qualities entitle it to rank among the most valuable ingredients in dyeing.

A strong decoction of this wood has a deep yellow-red colour; when diluted with water, it becomes orange-yellow. The acids make this liquid turbid, with some inconsiderable differences; a slight greenish-yellow precipitate falls, and the supernatant liquid is of a pale yellow. The alkalies redissolve the precipitate, and give the liquor a deep reddish colour.

This is the colour which alkalies give to the decoction of fustic; they render it deeper and almost red. There is formed,

with time, a deposite of a yellowish substance, which adheres to the vessel, and sometimes floats on the top.

Alum forms a small quantity of a yellow precipitate; the liquor remains transparent, and of a less deep yellow.

Alum and tartar together, afford a precipitate which has the same colour, but it is slower in falling. The liquor retains a still deeper hue.

The muriate of soda makes the colour a little deeper, without occasioning turbidity.

Sulphate of iron forms a precipitate at first yellow, but which grows more and more brown; the liquor continues brown, and without transparency.

Sulphate of copper affords an abundant precipitate of a brown-yellow; the supernatant liquor retains a feeble greenish colour.

Sulphate of zinc yields a greenish-brown precipitate; the liquor retains a reddish-yellow colour.

Acetate of lead forms an abundant orange-yellow precipitate; the liquor is transparent, and of a very faint greenish-yellow.

The solution of tin gives a very copious precipitate of a fine yellow, a little brighter than the preceding; the liquor retains a faint yellow colour.

For use, yellow wood is cleaved into splinters, or, what is better, reduced into chips or powder; it is then enclosed in a bag, to prevent some portions of it from fixing on the stuff and tearing it.

Weld gives to cloth which has received no preparation, only a pale yellow, which does not long resist the action of the air; but yellow wood produces, without the aid of mordants, a yellow colour, bordering on brown, which, though dull, resists the air better. Vivacity is given to its colour, and its permanence is augmented, by the mordants employed for weld, which exercise on it an action altogether analogous: thus alum, tartar, and solution of tin, render its colour brighter; sea salt and sulphate of lime deepen its hue. The processes which have been pointed out for weld, may therefore be applied to fustic, with this difference, that in order to obtain the same shade, much less yellow wood must be employed. Thus, from 5 to 6 parts of this wood are sufficient to give a lemon colour to 16 parts of cloth. The colours, however, obtained



by these processes, incline more to orange, and are duller than those of weld. Occasionally, the two are mixed, according to the effect wished to be obtained.

To Chaptal we owe an easy means of procuring from fustic a livelier colour. Having remarked that the decoction of this wood gave a precipitate with gelatin, and that a fine yellow colour was then obtained from it, he prescribes, "to boil in the bath of yellow wood, parings of skins, glue, or other animal matters; and then, without filtering, the stuff is to be worked in it, which will thus take the most beautiful and intense colour."\*

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### CHAPTER III.

#### *Of Quercitron.*

To Bancroft we are indebted for this dye-stuff. He has given an ample description of its properties, and of the uses to which it is adapted. We shall here exhibit a summary account of them.

Quercitron is the bark of the *Quercus nigra* of Linnæus. The epidermis, which yields a brownish colour, must be separated carefully from the bark; after which this is reduced to powder in a mill.

This powder affords as much colouring matter as 8 or 10 parts of weld, and 4 of fustic. Its colour possesses a great analogy to that of weld, but it is much cheaper.

Quercitron readily yields its colouring matter to water merely tepid. An extract is obtained from it, amounting to 1-12th the weight of the bark; but it is difficult to employ this in dyeing, because if a boiling heat be used, its colour becomes brownish; and if the evaporation takes place slowly, it suffers another kind of alteration.

The decoction of quercitron is of a brownish-yellow colour. The alkalies deepen, and the acids brighten it. The solution of alum separates a very small portion of its colouring matter, which forms a deep yellow precipitate. The solutions of tin

\* Mem. de l'instit. tom. i.

produce a more copious precipitate of a lively yellow. Sulphate of iron affords a plentiful precipitate of a deep olive colour; the supernatant liquor is clear, and of a light olive-green.

For dyeing wool, it is sufficient to boil the quercitron with its own weight, or one-third more than its weight, of alum, for two minutes. The stuff is then introduced, and the deepest shades are given at first, ending with straw colour. These colours may be brightened, by passing the stuff on quitting the bath through hot water, whitened with a little washed chalk. But the colour obtained by this process is not so permanent as when the stuff is subjected to a *bouillon* before passing it through the dyeing bath. In this second method, the stuff is boiled for an hour, or an hour and a quarter, in a solution of alum, containing one-sixth or one-eighth of the weight of the wool. No tartar should be used. It is next dyed in a bath prepared with a weight of quercitron equal to that of the alum employed, till the colour be sufficiently raised. Chalk being now introduced into the bath to brighten the colour, the stuff is let down anew for 8 or 10 minutes.

A brighter colour is obtained by means of solution of tin. Bancroft directs us to employ for the bath an equal weight of quercitron and solution of tin in nitro-muriatic acid, (or rather in the mixture of nitric and sulphuric acids, of which we have spoken in treating of scarlet.) When a brilliant golden-yellow colour is wanted, verging on orange, only 7 or 8 parts of solution of tin are employed for 10 of quercitron and 5 of alum. A little tartar added to these ingredients gives a lemon colour, bordering on green, which has hitherto been thought to be obtainable only by weld.

Quercitron may be substituted for weld, for the different shades given to silk, which should first be alumed. The dose is from 1 to 2 parts of quercitron for 12 of silk. The colour may be brightened by adding a little chalk or potash towards the end of the operation. The solution of tin may also be used along with alum, which should be in larger proportion.

In the substitution of quercitron for weld in calico printing, Bancroft prescribes, after the preliminary operations of printing, to diffuse the powdered quercitron in cold water, to introduce the pieces to be dyed, and to heat the bath by degrees, turning the cloth slowly round the winch. The colour is livelier and

more durable, if the heat be raised only a little above the temperature of the human body, than when it approaches nearer to ebullition. The intensity of the yellow may be varied, either by increasing the proportion of quercitron, or by prolonging the immersion. One advantage of this article over weld, is its scarcely colouring the white grounds when the heat of the bath has not been too much raised. Hence washing with cold water, and especially with hot water, suffices, without its passage through bran, and without exposure on the grass. From the difference between the temperatures which quercitron and weld require, the mixture of these two articles can produce no good effect. The addition of tartar increases the property possessed by quercitron, of not altering the white grounds. It makes the colour verge towards that green shade which causes weld to be sought after; but in this case the heat of the bath must be raised a little higher.

Bancroft describes a topical colour, which is obtained from quercitron. A strong decoction of quercitron is made, filtered, and evaporated at a gentle heat, and when it is reduced to less than one-half, it is allowed to cool to the temperature of the living body. After this, one-fourth of acetate of alumina is mixed with this liquid. The mixture is thickened with as much gum as is necessary to prevent its running during the impression, but not so much as to obstruct its penetrating the stuff. The colour obtained by this application has neither as much intensity, nor as much permanence, as that procured by previously impregnating the stuff with the mordant. Both qualities may however be increased by a mixture of nitrate of copper and nitrate of lime.

Quercitron ought undoubtedly to be considered as a very useful substance in dyeing; yet the attempts which we know to have been made, with the precautions prescribed by Bancroft, especially in reference to the temperature of the bath, seem to us to prove, that the colour derived from it is inferior in permanence to that producible from weld. A purer and more lively colour may be obtained from quercitron, by adopting the process which Chaptal has given for fustic, (yellow wood).

## CHAPTER IV.

*Of Annatto (Rocou.)*

ANNOTTO (in French *rocou* or *roucou*,) is a somewhat dry and hard paste, brown without, and red within. It is usually imported in cakes (of two or three pounds' weight,) wrapped up in leaves of large reeds, packed in casks, from America, where it is prepared from the seeds of a certain tree, the *bixa orellana* of Linnæus.

We are indebted to Leblond for some accurate observations concerning the cultivation of the tree whose seed serves for making annatto, the preparations to which these are subjected, and the means of improving this process.\*

The pods of the tree being gathered, their seeds are taken out and bruised. They are then transferred to a vat, (which is called the steeper,) where they are mixed with as much water as covers them. Here the substance is left for several weeks, or even months; it is now squeezed through sieves placed above the steeper, that the water containing the colouring matter in suspension may return into the vat. The residuum is preserved under the leaves of the banana (pine apple) tree, till it becomes hot by fermentation. It is again subjected to the same operation, and this treatment is continued till no more colour remains.

The substance thus extracted is passed through sieves, in order to separate the remainder of the seeds, and the colour is allowed to subside. The precipitate is boiled in coppers till it be reduced to a consistent paste; it is then suffered to cool, and dried in the shade.

Instead of this long and painful labour, which occasions diseases by the putrefaction induced, and which affords a spoiled product, Leblond proposes, simply to wash the seeds of annatto till they be entirely deprived of their colour, which lies wholly on their surface, to precipitate the colour by means of vinegar, or lemon juice, and to boil up in the ordinary manner, or to drain in bags, as is practised with indigo.

The experiments which Vauquelin made on the seeds of annatto imported by Leblond, confirmed the efficacy of the pro-

\* Ann. de chimie, tom. xlvii.

cess which he proposed, and the dyers have ascertained, that the annotto obtained in this manner was worth at least four times more than that of commerce; that, moreover, it was more easily employed; that it required less solvent; that it gave less trouble in the copper, and furnished a purer colour.

Annotto dissolves better and more readily in alcohol than in water; whence it is introduced into the yellow varnishes for communicating an orange tint.

The decoction of annotto in water has a strong peculiar odour, and a disagreeable taste. Its colour is yellowish-red, and it remains a little turbid. An alkaline solution renders it orange-yellow, clearer, and more agreeable; while a small quantity of a whiteish substance is separated from it, which remains suspended in the liquid. If annotto be boiled in water along with an alkali, it dissolves much better than when alone, and the liquid has an orange hue.

The acids form with this liquor an orange-coloured precipitate, soluble in alkalies, which communicate to it a deep orange colour. The supernatant liquor retains only a pale yellow colour.

Solution of muriate of soda and muriate of ammonia produce no sensible change.

Solution of alum causes a considerable precipitate of a deeper orange hue than the deposit formed by the acids; the liquid retains an agreeable lemon colour, verging a little towards green.

Sulphate of iron forms an orange-brown precipitate; the liquor retains a very pale yellow colour.

Sulphate of copper affords a precipitate of a yellowish brown; a little brighter than the preceding; the liquor preserves a greenish-yellow colour.

Solution of tin produces a lemon-yellow precipitate, which falls slowly.

When annotto is used, it is always mixed with alkali, which facilitates its solution, and gives it a colour inclining less to red. The annotto is cut in pieces, and boiled for some instants in a copper with its own weight of crude pearl ashes, provided the shade wanted do not require less alkali. The cloths may be thereafter dyed in this bath, either by these ingredients alone, or by adding others to modify the colour; but annotto is sel-

dom used for woollen, because the colours which it gives are too fugitive, and may be obtained by more permanent dyes. Hellot employed it to dye a stuff prepared with alum and tartar; but the colour acquired had little permanence. It is almost solely used for silks.

For silks intended to become aurora and orange, it is sufficient to scour them at the rate of 20 per cent of soap. When they have been well cleansed, they are immersed in a bath prepared with water, to which is added a quantity of alkaline solution of annotto; more or less considerable, according to the shade that may be wanted. This bath should have a mean temperature, between that of tepid and boiling water.

When the silk has become uniform, one of the hanks is taken out, washed, and wrung, to see if the colour be sufficiently full; if it be not so, more solution of annotto is added, and the silk is turned again round the sticks. The solution keeps without alteration.

When the desired shade is obtained, nothing remains but to wash the silk, and give it two beetlings at the river, in order to free it from the redundant annotto, which would injure the lustre of the colour.

When raw silks are to be dyed, those naturally white are chosen, and dyed in the annotto bath, which should not be more than tepid, or even cold, in order that the alkali may not attack the gum of the silk, and deprive it of the elasticity which it is desirable for it to preserve.

What has been now said regards the silks to which the aurora shades are to be given; but to make an orange hue, which contains more red than aurora, it is requisite, after dyeing with annotto, to redden the silks with vinegar, alum, or lemon juice. The acid, by saturating the alkali employed for dissolving the annotto, destroys the shade of yellow that the alkali had given, and restores it to its natural colour, which inclines a good deal to red.

For the deep shades, the practice at Paris, as Macquer informs us, is to pass the silks through alum; and if the colour be not red enough, they are passed through a faint bath of brazil wood. At Lyons, the dyers who use carthamus sometimes employ old baths of this ingredient for dipping the deep oranges.

When the orange hues have been reddened by alum, they must be washed at the river; but it is not necessary to beetle them, unless the colour turns out too red.

Shades may be obtained also by a single operation, which retain a reddish tint, employing for the annotto bath a less proportion of alkali than has been pointed out.

Guhliche recommends to avoid heat in the preparation of annotto. He directs it to be placed in a glass vessel, or in a glazed earthen one, to cover it with a solution of pure alkali, to leave the mixture at rest for 24 hours, to decant the liquor, filter it, and add water repeatedly to the residuum, leaving the mixture, each time, at rest for two or three days, till the water is no longer coloured; to mix all these liquors, and preserve the whole for use in a well-stopped vessel.

He macerates the silk for 12 hours in a solution of alum, at the rate of an eighth of this salt for one part of silk, or in a water rendered acidulous by the aceto-citric acid above described; and he wrings it well on its coming out of this bath.

Silk thus prepared is put into the annotto bath, quite cold. It is kept in agitation there till it has taken the shade sought for; or the liquor may be maintained at a heat far below ebullition. On being taken out of the bath, the silk is to be washed, and dried in the shade.

For clearer hues, a liquor less charged with colour is taken; and a little of the acid liquid which has served for the mordant may be added, or the dyed silk may be passed through the acidulous water.

If the last shades are to have less of the orange, and to approach the colour of nankeen, a little of the solution of nut-galls, in white wine, is to be added.

To give an orange colour to cotton, Wilson directs us to bruise the annotto when it is moistened, to boil it in water with double its weight of alkali, to let it settle for half an hour, to pass the clear liquor into a heated vessel, and to immerse the cotton in it, when it will take an orange colour. A hot solution of tartar is to be then poured into the bath, so as to make it feebly acid; the cotton hanks are turned through it on the skein-sticks, or wound on the winch when in the piece. The colour becomes thereby more lively, and fixes better. A slight

washing is afterwards given to the cotton, and it is dried in a stove.

We have seen the following preparation employed for cotton velvet. One part of quicklime, one of potash, two of soda. Of these a ley is formed, in which one part of annotto is dissolved; and the mixture is boiled for an hour and a half. This bath affords the liveliest and most brilliant auroras. The buff (chamois) fugitive dye is also obtained with this solution. For this purpose only a little is wanted; but we must never forget that the colours arising from annotto are all fugitive. (NOTE R.R.)

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## CHAPTER V.

*Of Saw-wort (Sarette), Serratula Tinctoria, and several other Articles capable of dyeing Yellow.*

THE *serratula tinctoria*, saw-wort, is a plant which grows abundantly in woods and meadows. It affords, without mordants, a greenish yellow colour, which wants permanence; but by means of alum employed in a particular *bouillon*, or put into the bath with the saw-wort itself, this plant gives a permanent and agreeable colour. According to Poerner, the mordants that suit it best are alum and sulphate of lime. It is needless to state, that the last article forms a deeper shade, and that the hue may be varied also by the proportion of mordant and of saw-wort. Scheffer directs us to prepare the wool with alum and a 12th of tartar; and adds, that if prepared with 3-16ths of solution of tin, and as much tartar, it takes a much livelier colour than the preceding.

Dyer's broom, or dyer's weed, (*genista tinctoria*, the *genestrole* of the French,) which grows abundantly in dry and hilly grounds, yields a yellow colour, which cannot be compared in beauty with that of weld and saw-wort, but it acquires sufficient permanence by means of mordants. Those which may be employed with most advantage, either for the preparation of the cloth or in the bath, are tartar, alum, and sulphate of lime.

Chamomile, (*camomilla matricaria*,) a plant well enough



known, affords a pretty agreeable faint yellow colour, but it is not fast. The mordants fix it a little; of which the most useful are alum, tartar, and sulphate of lime.

According to Scheffer, a beautiful yellow is given to silk with the decoction of this plant, in which some solution of tin, saturated with tartar, is poured, drop by drop, till the colour shall become sufficiently yellow. For dyeing the silk, this is kept hot without boiling. He recommends the employment of pure water, which does not precipitate the solution of tin.

*Fenugreek* (*trigonella fœnugræcum*) produces seeds, which, when ground, are capable of dyeing a pretty fast pale yellow. The mordants which succeed best with this substance, are alum, and muriate of soda.

The *turmeric* (*curcuma longa*, *terra merita* of the French) is a root imported from the East Indies. It has been cultivated at Tobago; and some of it sent thence was superior to that of commerce, both in the thickness of its roots and the abundance of its colouring matter. This substance is very rich in colour, and no other affords so brilliant an orange-yellow. But it has no permanence, nor can mordants give a sufficient degree of it. Muriate of soda, and muriate of ammonia, are the substances which best fix this colour, but they deepen it, and make it incline to brown. Some persons recommend a small quantity of muriatic acid. For employing this root, it must be reduced to powder. It is sometimes used for giving yellows made with weld a gold cast, as also for giving an orange hue to scarlet; but the shade arising from the turmeric is not long of disappearing in the air.

*Fustet* Venus's sumach (*rhus cotinus*) is a wood possessing a mixed colour of orange and green. Its fibres have a play of colours.

This wood affords a fine orange colour which has no permanence; hence it is not employed alone, but is used by mixing it with other colouring substances, and particularly with cochineal, to give the scarlet a flame colour, and for pomegranates, *jujubes*, lobster-reds, oranges, *jonquilles*, golden colours, buffs, and, in general, for all the colours with which we wish to associate more or less of an orange hue. The advantage to be found in the use of this substance, consists in its colour becoming pale without change of shade; but when it is joined with other colours, it is more durable than when alone.

The grain of *Avignon*, French berries, (the berry of the *rhamnus infectorius*, *épine cormier* in French,) which is gathered before it is ripe, affords a pretty fine yellow, but it has no permanence. It may be used by preparing the cloth in the same way as for dyeing with weld. As this berry is rich in colour, it is often substituted for weld in calico-printing, although it is inferior in quality.

The leaves of willow are mentioned by Scheffer as capable of yielding a fine yellow colour to wool, silk, and linen. Bergmann says, that the leaves of the laurel willow should be preferred, (*salix pentandra*), and that the leaves of common willow afford a colour, most part of which is soon discharged by the sun.

Scheffer directs the wool to be left for a night in a cold solution of one-fifth of alum, and one-sixteenth of tartar. The *bouillon* is made from the leaves picked up towards the end of August or the beginning of September, which have been dried in a shady, but well-aired situation. Of these a suitable quantity is to be taken, and boiled for half an hour, 1-256th part of white potash is added to it, to render the colour livelier and deeper, after which the bath is passed through a sieve. It is kept in a state approaching to ebullition, and the wool is died in it, till it has assumed the wished-for colour. He prescribes the same process for silk and linen, augmenting merely the proportion of alum by a sixteenth. According to Bergmann's account, Alströemer observed, that the colour was rendered richer by macerating the flax with a larger quantity of alum, and wringing and drying it before dyeing; and that for the complete extraction of the colouring matter, it was requisite to increase the quantity of potash.

The bark, and particularly the young branches (shoots) of the Italian poplar, and some other species of poplar, give to wool, according to d'Ambourney, a fine durable yellow colour, especially when the wool has been prepared with solution of tin. Nearly seven parts in weight of this wood are required to dye one of wool.

The seeds of purple trefoil (*trifolium pratense purpureum majus Raii*) are employed in Switzerland and in England for dyeing. Vogler has tried to determine what colours can be procured from it, and he found, that the bath of this seed, with

solution of potash, afforded a very deep yellow; with sulphuric acid, a clear yellow; with solutions of alum and tin, a lemon yellow; with sulphate of copper, a greenish-yellow. Woods impregnated with these mordants, and boiled for some minutes in the bath of purple trefoil seed, are found to be dyed very durably different shades of the colours just enumerated. The yellows form a fine green with indigo. Luzern (*medicago sativa*) afforded the same results.\*

Dizé made comparative experiments with the trefoil and weld.† It thence follows, that the trefoil seed gives to wool a beautiful orange-yellow, and to silk a greenish-yellow; that solution of tin cannot be employed for this dye, because it requires an aluming; and, lastly, that blue applied to the yellow derived from trefoil seed, forms a less beautiful and duller green than that for which weld had been used.

Common Canada golden rod (*solidago canadensis*) had already been recommended by Hellot. Gaad said, in the Memoirs of Stockholm, that this plant afforded a yellow colour, superior even to weld, and that it was far preferable to dyer's broom. As no use has been made of it, however, and as it is a plant easily cultivated, Succow subjected it to new trials.‡ As his experiments with re-agents presented nothing peculiar, they may be omitted. A decoction of the stalks of this plant, to which the author added a considerable proportion of alum, gave to a pattern of cloth, which had received no preparation, a very lively straw-yellow colour; to another pattern, prepared with sulphate of iron, a greenish-yellow colour; and to a third pattern, which had been prepared with alum, a very pure and lively lemon-yellow hue.

The flowers of French Marygold (*tagetes patula*) separated from their calyx, were submitted to the same trials. The cloth, without preparation, took in the decoction of these flowers a deep yellow colour; prepared with sulphate of iron, a greenish colour, which, by continued ebullition, became very deep; and, lastly, cloth prepared with alum assumed a very lively yellow colour, inclining a little to green. If a little alum be added to the bath before immersing the stuff in it, a very beautiful and

\* Annales de chimie, tom. iii.

† Journ. de physique, 1769.

‡ Crell. Ann. chem. 1787.

lively yellow is obtained. It has more lustre than even the colour procured from the Canada golden rod.

There are many other substances which may be employed for dyeing yellow, and which afford shades of greater or less permanence and beauty; such are the bark of the barberry, the flower of wild chervil or cow-weed, the common stinging nettle, the root of patience-dock, the bark of the ash, the leaves of the almond tree, of the peach tree, pear tree, the flowers of the common furze, &c. In Part I. it was shown that nitric acid could also be employed for giving a yellow colour.

White flowers, according to the observation of Lewis, give the water with which they are boiled a somewhat deep yellow colour. The acids, alkalies, and the salts, act upon this colour as those of other vegetable substances.\*

It appears that the substances which may be used for dyeing yellow are very numerous. They differ from each other in the quantity of colouring matter, in their dye being more or less plain, lively, or of an orange or greenish cast, in their degree of permanence, and in their price. By comparing these particulars, a determination is to be made as to their choice, according to the quality of the stuff, the colour that is wanted, and the concomitant circumstances.

In general, the alkalies render the colour of these substances deeper and more of an orange cast; they facilitate the extraction of the colouring matter; and it is only by their means that it is obtained from annatto; but they also favour its destruction. Sulphate of lime, muriate of soda, muriate of ammonia, deepen the colour of yellow substances; the acids brighten them, and make them more permanent. Alum and the solution of tin render them clearer, and at the same time more brilliant and durable.

Few of the yellows produced from vegetable substances can acquire upon cotton permanence comparable to that of the colours producible from madder; and they never acquire this quality without losing their lustre. When a colour rather fast than brilliant is wanted, the cotton is coloured with oxyde of iron, by impregnating it with any of the various solutions of this

\* The Chemical Works of Caspar Neuman.

metal. The processes employed for this dye are very numerous, and their shades may obviously be greatly multiplied, by varying the state of oxydation of the metal, or the nature of the acid which holds it in solution; as also by slight changes in the proportions of the materials, and in the manipulations.

In order to obtain a deep colour, Chaptal treads the cotton in a solution of sulphate of iron, marking from  $17^{\circ}$  to  $23^{\circ}$  Twaddel. He squeezes it very slightly, but equably. As soon as the whole portion (lot) is dipped, it is repassed, hank by hank, through the same solution, and immediately afterwards through a solution of potash, marking the same number of degrees. The colour of the cotton becomes of a dirty blue-green, which changes in a few minutes to an agreeable golden yellow. At each dipping the vessel into which the cottons are plunged must be emptied, in order that the colour may be equal and uniform.

For a pale and very soft yellow, he treads the cotton in a solution of sulphate of iron, marking three degrees, and repasses it as in the preceding process. On the other hand, he prepares a liquor with solution of potash, marking from two to three degrees, to which he adds solution of alum till he observes that the flocks are no longer dissolved. He impregnates the cotton with this liquid, and renews it for each dip. The cotton is dyed of a very agreeable yellow.

When the colours are not sufficiently deep, the cotton may be repassed through stronger solutions.

Chaptal recommends for making the colours evenly, to pass at once no more than half a pound of cotton, to employ weak solutions of sulphate of iron, to dip the cotton first in a solution of potash, then in one of sulphate of iron, repeating these alternate dips as often as shall be requisite to arrive at the desired shade, and to use the greatest care in impregnating and squeezing the cotton equably.

A fresh-butter yellow is produced, by passing the cotton through slightly oxydized acetate of iron, mixed with nitrate of iron, which may be made to incline more to red, the greater the proportion of the latter salt.

With nitrate of iron alone diluted with water, a pretty clear yellow may be had, which rises quickly. If the cotton be impregnated with nitrate of iron a little diluted, allowed to dry,

and then washed, it remains a very deep tint, similar to that of rust.

The rust-yellow, which is printed on cloth, is made with two parts of sulphate of iron, and one part of acetate of lead. By mixing with this, different proportions of highly oxydized oxyde of iron, shades bordering on red may be procured.

Cotton dyed by these processes takes very different colours in the dye-baths. That which received a faint yellow colour by the process of Chaptal, becomes of a walnut hue in the decoction of galls. When the colour is deeper, it becomes mouse-grey; with tan or quercitron, it affords a yellow. When passed through a decoction of equal parts of nut-galls, sumach, log-wood, and weld, the cotton becomes of a dirty grey-white. When dried, and passed through a strong solution of sulphate of iron, it assumes the blueish grey colour, which is called *cail de roi*. NOTE SS.

## SECTION V.

### OF DUN, ROOT, OR FAWN COLOUR, (FAUVE.)

ONLY some of the substances employed for producing dun colours will be treated of, because their number is too great to be examined in detail; and they resemble one another sufficiently in their characters to render the observations made on a few applicable to the whole.

## CHAPTER I.

### *Of Walnut Peels.*

It is known that walnut peels are white interiorly, but when exposed to the air, they become brown, and then black. Hence, if the skin has been impregnated with its juice, it soon assumes a brown, and almost black colour.

If the internal part of fresh walnut peels be plunged into chlorine, it becomes brown in like manner.

The filtered decoction takes a deep brown colour in the air; it yields pellicles on evaporation, which when separated, well washed, and dried, are nearly black. The liquor freed from these pellicles yields a brown extract, which may be completely redissolved in water; but by a new evaporation it still affords pellicles similar to the first.

These pellicles, which are formed in several other evaporations, are derived from the colouring substance, whose properties have been changed from an increase in the proportion of carbon, by an agency which has been elsewhere explained.

Alcohol precipitates the colouring matter of the decoction of walnut peels in the form of a brown substance, which may be redissolved in water.

The solution of potash produces at first no sensible change in

the decoction of walnut peels; but by degrees it becomes a little turbid, and its colour deepens.

Muriatic acid brightens up its colour, turning it yellow; there is formed a small quantity of a brown precipitate, and the liquor remains of a clear yellow.

Solution of tin produces an abundant precipitate in the decoction of a dun ash-colour; the liquor retains only a faint yellow hue.

Solution of alum disturbed the liquor slightly; a very small deposit was formed of a dun brown. The liquor preserved a clearer colour, but still dun.

Solution of sulphate of copper disturbed the liquor but very slowly; a scanty green-brown precipitate was formed. The supernatant liquid remained green.

Acetate of lead speedily formed an abundant deposit of a deep dun colour.

Solution of sulphate of iron rendered the colour much deeper, and even black. On diluting it with water, it passed through brown to greenish-dun, but it let fall no deposit.

Solution of pure sulphate of zinc disturbed the liquor but slightly, rendering the colour thereby deeper.

The decoction of walnut root presented nearly the same properties. On separating the bark from the ligneous substance of this root, the former yielded in equal weight a liquor much more charged with colour. The bark of the wood of walnut also exhibited properties approaching to those of walnut peels, but its decoction formed a blackish precipitate with sulphate of iron.

Walnut peels exercise a lively action on oxyde of iron, dissolving it, and forming a liquor as black as ink. If boiled along with clean filings, they do not attack them, but if left exposed to the action of the air, the liquor becomes soon black.

The colouring matter of walnut peels has a great disposition to combine with wool. It gives it a very durable walnut or dun colour, and mordants appear to add little to its permanence, but they may vary its shades, and give them more lustre. By preparing the stuff with alum, a richer and livelier colour may be obtained.

Walnut peels are of excellent use, because they give agree-



able and very durable shades ; and being employed without any mordant, they preserve the softness of the wool, and require but one simple and not expensive operation. Walnut peels are gathered when the nuts are entirely ripe. Large casks or tubs are filled with them, and a sufficiency of water is poured on them to cover their surface. In this state they may be kept a year and upwards. At the Gobelins, where a very extensive and varied use is made of this ingredient, it is kept for two years before it is employed. It is found then to furnish much more colour. It has a very unpleasant putrid odour.

The peels may also be used which are taken from the nuts before they are ripe ; but they do not keep so long.

When it is wished to dye with walnut peels, they are boiled for a full quarter of an hour in a copper, in quantity proportioned to the amount of stuff, and to the depth of shade that is desired. For cloths, the deepest shades are usually begun with, finishing with the lighter ones ; but for woollen yarn, it is commonly the clearest shades that we begin with, and the deepest shades are made at the end, with the addition of husks for each parcel. The woollen cloth and yarn ought to be simply moistened with tepid water, before being plunged in the copper, in which they are turned about with care till they have assumed the desired shade, unless a preliminary aluming be given.

The root of walnut gives the same shades, but for this effect the quantity must be increased. It must be reduced to chips ; and it is proper to enclose it in a bag, to prevent the little chips from sticking to the stuff. The colour becomes often unevenly with the formation of spots. To obviate this inconvenience, the fire must be tempered at the beginning, that the colouring particles may be equally distributed through the bath, in proportion as they are extracted from the root. If some parts be unequally dyed, as the colour is fast, there is no method of remedying this accident except to reserve the stuff for deeper colours.

## CHAPTER II.

*Of Sumach, and some other Substances capable of affording a Dun Colour.*

COMMON sumach (*rhus coriaria*) is a shrub which grows naturally in Syria, Palestine, Spain, and Portugal.

It is diligently cultivated in Spain and Portugal. The shoots are cut down to the root every year, then dried that they may be ground to powder in a mill. This powder is employed by dyers and tanners. The name of *rédioul* or *roudou* is given to the sumach cultivated in the neighbourhood of Montpellier.

The infusion of sumach is of a dun colour, bordering on green. It speedily becomes green in the air. When it is recent, the solution of potash produces little change on it. The acids clear up its colour, and render it yellow. Solution of alum makes it turbid, producing a scanty yellow precipitate, while the liquor remains yellow.

Acetate of lead forms instantly an abundant yellowish precipitate, which takes a brown colour on its surface; the liquor remains of a clear yellow.

Sulphate of copper affords a copious yellowish-green precipitate, which, after some hours, changes to a brown-green. The liquor remained clear, and a little yellow.

Sulphate of zinc of commerce rendered the liquor turbid, blackening it, and forming a deep blue precipitate.

Pure sulphate of zinc deepened the colour much less; only a slight dun deposit verging on brown took place.

Muriate of soda produced no sensible change at first; but after some hours, the liquor was a little turbid, and its colour had become somewhat clearer.

Sumach acts like nut-galls on solution of silver, whose metal it reduces; a result promoted by the action of light. We have already dwelt at sufficient length on the explanation of this phenomenon, as well as the general properties of astringents.

Sumach affords, of itself, a dun colour bordering on green; but it communicates to cotton stuffs several very permanent colours when they are combined with mordants.

Thus, as we have already stated, it yields a black with acetate of iron, if this has been printed on it in a state of concentration, but shades of grey if it has been diluted with water. With acetate of alumina it gives a durable yellow, which retains somewhat of a greenish shade; hence, if into the same pattern, yellow, grey, and black colours are to be introduced, they may all three be given by sumach.

To dye with this substance, the water must be heated to about 145° Fahr., the sumach is then to be thrown in, and the cloths immediately introduced, leaving them immersed only 15 or 20 minutes, with a slight elevation of the heat of the bath. If the heat be too much raised, and if the cloths be left too long in the boiler, the colours will become weaker instead of stronger; and even, in a little time, those that have iron for their mordant disappear almost altogether. This effect, which occurs in a less remarkable degree with many other dyes, requires us to catch the very instant for withdrawing the cloths when the colours are sufficiently raised. To procure an evenly colour, only a small number of pieces should be dyed at a time.

Cloths dyed with sumach resume a fine white with difficulty, and are little improved by exposure on the grass. More effect is produced by passing them through water sharpened with so little sulphuric acid as to make it just perceptibly sour. By this means the greys lose the russet tint which they have on coming out of the boiler, and become agreeable. Blacks thereby acquire a great deal of lustre.

We have said, in treating of greys, that by alternately passing the cotton through a decoction of sumach, much diluted with water, and an equally dilute solution of iron, very agreeable shades of grey are obtained, whose intensity depends on the concentration of the bath, and the number of times that the operations are repeated. In general, to dye equably in this way, the colours must be slowly brought up, beginning with very feeble baths, passing repeatedly through each of them, and gradually increasing their strength when deep shades are wanted.

By finishing with the solution of sulphate of iron, the cotton has not that russet hue which it takes when sumach is last used, which it becomes necessary to remove with the acidulated water.

With concentrated solutions of sumach and sulphate of iron,

the cotton assumes a black colour when it has been turned three or four times through each of them; and if, on issuing for the last time from the sulphate of iron, it be passed through a tepid decoction of logwood, to which a little acetate of copper is added, the black becomes brilliant and sufficiently fast. The cotton is softened and the black heightened, by passing it through hot water into which a little oil has been poured.

If, in dyeing grey, the decoction of logwood be mixed with that of sumach, the grey becomes slate coloured; if after this it be passed through a very dilute decoction of weld, mingled with alum, it inclines towards pearl-grey.

By substituting nut-galls for sumach, other shades are obtained.

Cotton thus treated with the decoction of logwood and with sulphate of iron, affords slate-greys of little permanence.

Decoction of quercitron produces American grey; and if a little alum and muriate of tin be mixed with it, instead of that colour, an American green is produced.

With yellow wood, (fustic,) alder bark, &c. other colours are obtained. By thus varying the colouring matters, and making use of sulphate of iron and alum, or muriate of tin, and combining variously the order and number of the operations, as well as the concentration of the baths, a great many shades may be obtained on cotton, which are generally pretty fast.

This manner of dyeing, by passing alternately through the mordant and colouring matter, is of advantage for procuring uniform colours; and it further presents great facilities for attaining the wished-for shade, and for diversifying those produced.

Birch tree bark, *betula alba*, (*l'aune* of Berthollet,) affords a decoction of a clear dun hue, which becomes speedily turbid, and brown in the air. It forms with solution of alum a pretty copious yellow precipitate; and with solution of tin, an abundant precipitate of a clear yellow. It blackens the solutions of iron, forming with them a tolerably copious precipitate; hence it contains much of the astringent principle. It dissolves a large quantity of the oxyde of iron; thence the use made of it in the black vats, destined for dyeing (linen) yarns. It does not, however, possess the property of dissolving the oxyde of iron in the same degree with the decoction of walnut peels.

Much use is made for ordinary stuffs in the East, of the leaves of a shrub called Henna, (*Hhenne*,) which is of the family of *Salicaria*. It was known to the ancients by the name of *Ciprus*, and was employed for dyeing the envelopes of mummies, in which its colour is still observable.

The leaves of this shrub, now cultivated in Egypt, are bruised, after being hastily dried. A paste is then made of them, which is used for dyeing the nails and the palms of the hands of a reddish dun, (a tawny hue.)

The powder of these leaves has an olive colour; it yields by boiling with water a very deep orange dun, very rich in colouring matter.

Almost all vegetables contain, especially in their bark, more or less colouring matter, capable of affording dun hues, inclining to yellow, brown, red, or green. These colouring matters present greater or less differences among each other, in reference to their quantity and quality; they further vary according to climate and the age of the vegetable. A great diversity of shades, therefore, may be procured, by modifying the dun natural to the vegetables, by means of different mordants. This has been accomplished by Siefferts,\* and particularly by D'Ambourney.† Thus in a great many experiments which the latter made, employing the parts of different vegetables, and using different mordants, the colours which he produced were, for the most part, between yellow and brown, such as *carmelites*, olives, cinnamons, and chestnuts.

The decoction of the greater part of vegetables, and especially of barks, affords a colour, differing only in shade, and exhibits with re-agents nearly the same characters: it forms a yellow precipitate more or less deep with alum, and a clearer colour with solution of tin. It acts on solutions of iron as an astringent. The decoction of walnut peels, however, produces a peculiar effect with solutions of iron; it assumes a very deep colour, but no precipitate is formed even after two or three days. Their decoction, as well as that of walnut tree bark, has a powerful action on oxyde of iron; it saturates it, forming a black liquor; and even if filings of iron be put into this decoc-

\* Versucht mit einheimischen Farbe Materien.

† Recueil des procédés et d'expériences sur les teintures solides, que nos végétaux indigènes communiquent aux laines et aux lainages.

tion exposed to the air, in two or three days it forms a black liquor by means of the oxygen which it attracts from the atmosphere. But if a decoction to which solution of sulphate of iron has been added, be boiled, an abundant black deposit instantly falls. It is only, therefore, in a trifling circumstance that walnut peels, as well as walnut tree bark, differ from the other substances which yield a dun colour; yet its extractive matter possesses in particular the property of becoming black by the action of the air, and the pellicles formed when it is evaporated, assume in a very marked degree the appearances of a carbonized substance.

If the yellow colour produced by several vegetable substances be compared with the dun which most of them afford, a close relation will be found between these colours. There are even some which may be referred equally to yellow and to dun. There are duns which, by means of alum and solution of tin, pass to yellow, and the yellow is very fast. The following distinction may be laid down. The yellows are in general more changeable, more apt to yield fugitive colours; for which reason the yellow colours must be fixed by means of mordants, whereas the most part of dun coloured substances afford by themselves a pretty permanent colour.

As the dun shades obtained from different substances vary to a great extent, sometimes several of these substances are blended in order to obtain a peculiar colour, and that in different proportions. Other ingredients are also mixed with them, to modify their colour and to render it faster.

Among these substances, there is still one which deserves attention; this is, sandal or sanders wood.

Three kinds of sandal wood are distinguished; the white sandal, the yellow, and the red. The last alone is employed in dyeing. It is a solid, compact, heavy wood, imported from the coast of Coromandel, which becomes brown on remaining exposed to the air. It is usually employed in the state of a very fine powder. It affords a colour dun, brown, and verging on red. By itself it furnishes little colour, and it is said to harden the wool. But its colouring matter dissolves better when mixed with other substances, such as walnut peels, sumach, nut-galls. Besides, the colour which it gives is permanent, and modifies advantageously the colours of the substances with which it is mixed.

Vogler, having observed that dilute alcohol or proof spirit dissolved the colouring matter of sandal wood much better than water, made use of this solution, either by itself or mixed with from 7 to 8 parts of water, for dyeing patterns of wool, silk, cotton, and linen, which he had prepared beforehand, by impregnating them with solution of tin, washing and drying them. These patterns took all a poppy-red colour. Patterns prepared likewise with alum, took a saturated scarlet colour; prepared with sulphate of copper, a beautiful clear crimson hue; prepared with sulphate of iron, a fine deep violet colour.\* He dyed cold with the spirituous liquor; but employed a slight ebullition for that which was mixed with water. This mixture takes place without the transparency being disturbed.

Soot is also employed for giving to wool a dun or brown colour, of greater or less depth according to the proportions of this ingredient; but soot gives only a fugitive colour, because it simply adheres to the wool, instead of combining with it. It hardens it, and leaves a bad smell. It is employed, however, in some respectable manufactories, for browning certain colours; undoubtedly, because shades are thereby obtained, which could be got with difficulty by other means.

\* Crell's Annals, 1790.

## SECTION VI.

### OF COMPOUND COLOURS.

SIMPLE colours form, by their mixture, compound colours; and, if the effects of the colouring particles did not vary, according to the combinations which they form, and the actions exercised on them by the different substances present in a dyeing bath, we might determine with precision the shade that ought to result from the mixture of two other colours, or of the ingredients which afford these colours separately: but the chemical action of the mordants, and of the liquor of the dye bath, often changes the results. Theory, however, may always predict these effects to a certain degree.

It is not the colour peculiar to the colouring matters which is to be considered as the constituent part of compound colours, but that which they must assume with a certain mordant, and in a certain dye bath. Hence, our attention ought to be principally fixed on the effects of the chemical agents employed.

It is in this department of dyeing that the intelligence of the operator may be most useful, by enabling him to vary his processes, and to arrive at the proposed end by the simplest, shortest, and least expensive way.

The processes for compound colours are very numerous. We shall mention only those which most merit attention, and shall establish the principle on which they ought to be conducted by particular examples. Several of the processes described in the course of this work afford compound colours. We shall now consider, in an especial manner, this part of the art of dyeing.



## CHAPTER I.

*Of the Mixture of Blue and Yellow, or Green.*

MANY different plants are capable of affording green colours; such as the field broom grass (*bromus secalinus*); the green berries of the berry-bearing alder (*rhamnus frangula*); wild chervil (*chærophylllum silvestre*); purple clover (*trifolium pratense*); common reed (*arundo phragmites*); but these colours have no permanence.

D'Ambourney says, however, that he has extracted a durable green from the fermented juice of the berries of the *rhamnus frangula*: he prepared the cloth with tartar, nitric solution of bismuth; and muriate of soda; and he added to the fermented and tepid juice of these berries a little acetate of lead. The cloth took, in this bath, an intermediate shade between parrot-green and grass-green.

Poivre, and some other writers, had announced, that there existed in different parts of India a green fecula, or a kind of green indigo, which would be precious to the dyer; but some trials of Bancroft seem to prove, that it was merely common indigo united to a yellow substance.

By mixture of blue and yellow, dyers form green, which is distinguished by a great number of shades. Address and experience are required for obtaining this colour uniform, and without spots, especially in the light shades.

The green may be formed by beginning the dyeing either with yellow or blue; but the first method has some disadvantages; for the blue soils the linen, and a portion of the yellow, dissolving in the vat, alters, or makes it green. The second method is preferred for woollen stuffs.

The pastel vat is usually employed; but, for some kinds of green, solution of indigo in sulphuric acid is used; in which case, the blue and yellow are separately dyed, or indeed all the ingredients may be mixed for dyeing at one operation. Finally, solutions of copper, with yellow substances, are had recourse to. We shall take a view of these different processes.

The blue ground which is given by the vat should be propor-

tioned to the kind of green that is wanted. Thus, for *verd canard*, the green like that of drake's neck, a deep blue is required; for parrot-green, a sky-blue ground; for *verd nascent*, nascent green, one of white-blue (*bleu blanchi*.)

When the cloths have undergone this operation, they are washed at the fulling-mill, and a *bouillon* is given them as in ordinary welding; but, for the lighter shades, the proportion of salts is diminished. More frequently the *bouillon* for cloths intended for light shades is first given; and, after taking them out, some tartar and alum are added: and this practice is pursued until we come to the cloths destined for the deepest shades, by the progressive addition of more tartar and alum.

The welding is conducted as for yellow; but a greater quantity of weld is employed, unless light colours alone are to be dyed, for which the proportion ought, on the contrary, to be less. Usually a succession of shades is dyed at the same time, from the deepest to the lightest; beginning with the deepest, and proceeding to the lightest. Between each dip, which lasts half an hour, or three quarters, water is added to the bath. Some dyers pass each parcel twice through each bath. They begin the first time with the deep shades, and the second with the light ones. In this case, each parcel should remain a shorter time in the bath. Care must be taken not to boil the bath for very light shades.

A browning is given to the very deep greens, with logwood and a little sulphate of iron.

It is still more difficult in silk than in cloth to prevent the green from being spotted and variegated. Silk intended for greens is boiled as for the ordinary colours; for light shades, however, it should be boiled thoroughly, as for blue.

Silk is not first dyed blue, like cloth; but, after a strong aluming, it is washed slightly in the river, and distributed into small hanks, that it may take the dye equally; after which it is turned carefully round the sticks, through a bath of weld. When it is thought that the ground is sufficiently deep, a pattern is tried in the vat, to see if the colour has the wished-for tone. If it has not ground enough, decoction of weld is added; and, when it is ascertained that the yellow has reached the proper degree, the silk is withdrawn from the bath, and passed through the vat, as for blue.

To render the colour deeper, and at the same time to vary its tone, there are added to the yellow bath, when the weld has been taken out, juice of brazil wood, decoction of fustet, and annotto. For the very light shades, such as apple-green and celadon-green, a much weaker ground is given than for the other colours. For the light shades, if not for sea-green, it is preferable to dye yellow in baths which have already been used, but in which there is no brazil wood or fustet, because the silk, perfectly alumed, dyes too rapidly in fresh baths, and is thence subject to take an unevenly colour.

For dyeing green in raw silks, those naturally white are selected, as for yellow; and, after being well soaked, they are alumed, and treated in the same way as the other silks.

When the blue vat is used for dyeing green, saw-wort may be employed instead of weld. It is even preferable, because the colour which it gives naturally inclines to green. Dyers' broom is also employed; and sometimes these two ingredients are mingled. Other substances which dye yellow may also be used; and a variety of shades may thus be procured.

The green obtained by means of solution of indigo in sulphuric acid, is known by the name of Saxon green. It has more brightness, but less permanence, than that just described. This process was first practised in Saxony, and government caused a description of it to be published in 1750.\* According to this description, the cloth must be boiled with alum and tartar for half an hour; it is then to be withdrawn, and aired, without washing. The bath is refreshed (with cold water), the solution of indigo is well mixed with it, pouring in at first only the half; the cloth is then let down, and turned rapidly through it, without boiling, for five or six minutes. It is lifted out, that the remainder of the solution may be poured in, which should be mixed with great care. The cloth, being slightly boiled for seven or eight minutes, is taken out and cooled. The bath is emptied to about 3-4ths, more or less, according to the shade of green that is wanted, and filled up with a decoction of fustic; and, when this bath is very hot, the cloth which had been dyed blue, and cooled, is passed through it, till it has acquired the wished-for shade. Cloth dyed blue in the bath with alum and

\* *Manière de teindre un drap blanc en vert, nommé vert de Saxe.*

tartar, has a less brilliant but more durable colour than when it is made blue without this mixture.

Experience has taught that this process may be executed in a more expeditious, and even more certain manner. The cloth is boiled as for welding, and then washed. Some fustic, reduced into chips, and enclosed in a bag, is put into the same bath. It is boiled an hour and a half; it is lifted up, and the bath is refreshed, so that the hand can be kept in it; about  $1\frac{1}{2}$  pound of solution of indigo is poured in for every piece of cloth 24 yards long which is to be dyed; this is to be turned through quickly at first, and afterwards slowly, and the cloth is lifted out before the bath boils.

It is a proper practice to pour in, at first, only 2-3ds of the solution, to lift up the cloth after two or three turns, and then to add the remaining third. The colour is thus rendered more uniform. If the colour seems not to take well, a little calcined alum, reduced to powder, is added. Saxon apple-green is dyed in the bath which has served for Saxon green, after a third or a half of it has been thrown out, and after it has been refreshed. The cloth is turned through it, till it approaches to ebullition.

It is easy to see that a great variety of greens may be produced, not only according to the proportions of the indigo and yellow dyes employed, but according to the nature of the yellow substance. For obtaining a decided green, however, fustic is preferred to the other colouring substances, because its colour is less affected by sulphuric acid, which clears up and impairs considerably that of the other substances.

In order to avoid this effect with the quercitron, Bancroft directs us to dye the stuff at first blue, to rinse it well in water, and give it afterwards a *bouillon* composed of three parts of washed chalk, and 10 or 12 of alum, for 100 of cloth. It is to be boiled for an hour. Then, without changing the bath, 10 or 12 parts of quercitron are introduced, and the dyeing is continued. At the end of a quarter of an hour, one part of chalk is added; and this addition is repeated at intervals of six or eight minutes, till a fine green colour is brought out.

Bancroft recommends, on several occasions, and other authors do the same, to add carbonate of lime to the sulphate of alumina (alum), for saturating the excess of acid in the latter; but it is merely the decomposition of a portion of the alum which is

thereby produced, and this decomposition is complete, if the proportion of carbonate of lime be sufficient. The carbonic acid is expelled; the alumina precipitates, retaining a little sulphuric acid; and the sulphate of lime falls down in part, and is in part held in solution, according to the quantity of water. The effect which lime, or carbonate of lime, produces on alum must not be confounded with that occasioned by potash or soda.

If a solution of alkali, deprived of carbonic acid, or even in the state of a carbonate, be poured, by portions, into a solution of alum, the small precipitate which occurs on the contact of the (alkaline) liquid is immediately redissolved; and it is only when the acidity is nearly saturated by the alkali, that the precipitate ceases to disappear. But the combination, even when neutral, retains a portion of alumina; and, when the precipitate has become permanent, it may be redissolved by a superabundance of alkali. It is obvious, therefore, that alkali can enter into combination with the sulphate of alumina (alum), and that a change may thus be introduced into it favourable to the operations of dyeing; whereas lime, and carbonate of lime, produce the immediate separation and precipitation of the alumina.

The sulphuric acid may be abstracted, in the process under discussion, by boiling the stuff that has been dyed Saxon blue, with carbonate of lime, before subjecting it to the *bouillon* of alum.

It is mentioned, as a fault in Saxon blue, that it has a greenish cast, proceeding probably from the slight alteration that sulphuric acid produces on the particles of indigo: it likewise, as well as Saxon green, is said to have less durability than the blues and greens obtained by means of the vat. It has been attempted in England to procure the lustre characteristic of Saxon blues and greens, by obviating the defects which accompany them, and by combining the advantages of the blue vat with those of the sulphuric solution of indigo. Gühliche describes a process for giving silk the English blue and green. These two objects are here united, to serve as examples of the different processes which may be practised.

He uses a cold vat for dyeing blue; and he extols it highly in respect of convenience, price, and beauty of colour.

This vat is composed of one part of indigo, three parts of

good quicklime, or lime slaked in the air, three parts of English vitriol, and one part and a half of orpiment. The indigo ought to be ground with care, and diffused in water, then put into a wooden vat, in which it is diluted with water to the proper degree, according to the intensity of colour that is wished for; the lime is now added to it; the mixture is well agitated, covered up, and left at rest for some hours. The vitriol, reduced to powder, is thereafter added; the vat is stirred well, and then covered up. After some hours, the orpiment, in powder, is thrown in; it is again left at rest for some hours; the mixture is now stirred, and then allowed to repose till the supernatant liquid appears clear, when the froth that covers its surface is put aside. The silk is now dyed in it hank by hank; but it must be previously passed through hot water. On coming out of the bath, it is washed in running water, and dried. When the bath becomes turbid, it is allowed to settle till it grows clear; an essential precaution for the light shades. When it begins to be exhausted, one-third of the ingredients is added to it, proceeding as at first. In proportion as the vat gets exhausted, the shades become lighter. This vat serves equally well for silk, linen, and cotton. Guhliche thinks that those persons who have not succeeded in dyeing silk with the cold vats, or who complain that only feeble hues are obtained, have been led into an error by employing too small a quantity of orpiment.\*

For English blue, a light blue must be first given to the silk. On being taken out of this bath, it is passed through hot water, washed in running water, and put into a bath composed of the sulphuric solution of indigo, to which a little solution of tin has been added, till it has assumed the desired shade, or has exhausted the bath. Before introducing it into this bath, it may be passed through a solution of alum, in which it must not be suffered to remain long. Silk dyed by this process has neither the reddish cast of the indigo vat, nor the greenish cast of Saxon blue.

To make English green, which is more beautiful than ordinary green, and more durable than Saxon green, Guhliche gives

\* Guhliche uses for wool, a vat composed of one part of indigo, four parts of potash, one part of quicklime, and a part and a half of orpiment. He follows the ordinary process, only he keeps this last bath at a moderate heat. He uses it also, in the same manner, for giving to cloth an English blue and green.

the silk. first of all, a clear blue in the cold vat; he steeps it in hot water; washes it in running water; passes it through a weak solution of alum; prepares a bath with the sulphuric solution of indigo, a little of the solution of tin, and a tincture of Avignon berry, made with a vegetable acid. He keeps the silk in this bath till it has assumed the wished-for shade; he then washes and dries in the shade. The lighter hues may be dyed in the sequel. The shades may be varied with more or less blue, more or less yellow, by the proportions of the indigo solution, and of the yellow substance. When it is wished to give a gosling-green (*verd d'oie*) to silk, a light blue is communicated to it, either in the hot vat or in the cold; it is passed through hot water, washed in running water, and, while moist, it is passed through a bath of annotto.

To give a green colour to linen and cotton yarns, it is proper to begin with scouring them well; then they must be dyed in the blue vat, cleansed in water, and passed through the weld process.

The strength of the blue and the yellow is proportioned to the colour that is wanted. As it is difficult to give uniformity to the cotton velvets in the ordinary blue vat, they are usually dyed yellow with curcuma (turmeric), and the green is produced with solution of indigo in sulphuric acid. It is of no consequence whether the blue or yellow be first given.

Le Pileur d'Apligny describes a process for dyeing of a water-green, or apple-green, by a single bath, cotton velvet as well as cotton hanks.

Verdigris is to be mixed with vinegar. The mixture is to be kept well corked for 15 days in a stove. Four hours before using it, there is added a solution of a quantity of crude pearl ashes, equal to that of the verdigris; and the mixture is kept warm. The yarn or the velvet is prepared by soaking in a hot solution of alum, at the rate of an ounce of this salt and  $8\frac{1}{2}$  pints of water to one pound. The stuff is lifted out, the verdigris liquor is added to the bath, and it is immersed again in order to be dyed.

All the shades of olive and drake's-neck green are made by giving to the yarns a blue ground, galling them, and passing them through the bath from the black cask,\* of greater or less

\* See page 227.

strength, then through the bath of weld with verdigris, and after this through a bath of sulphate of copper. Lastly, the colour is brightened by means of soap.

Chaptal obtains beautiful greens on cotton by the following processes. 1. He passes the cotton, dyed sky-blue, through a strong decoction of sumach, leaving it in it till the decoction be well cooled. He dries it, passes it through the mordant of acetate of alumina, dries again, washes, and works the cotton for two hours in a tepid bath, in which about  $26\frac{1}{2}$  pounds of quercitron have been infused for 110 pounds of cotton.

2. For 220 pounds of cotton, he mixes 110 pounds of alum, 22 of sulphate of copper, 22 of sulphate of iron,  $16\frac{1}{2}$  of acetate of lead, 3 of soda, and as much chalk. He passes the cotton dyed blue through this, then through lime water, and afterwards through a bath of quercitron.

Chaptal has remarked, that the yellow of weld unites ill with that of sumach, and that the mixture of their colours gives a bad tint to blue; but that, on passing the cotton afterwards through a ley marking 12 degrees, the colour becomes uniform, and is pretty fast. The colour of weld unites perfectly to that of tan. He prefers, however, to dye cottons intended for green in a blue vat, mounted with sulphuret of arsenic (orpiment), because it is difficult to obtain a fine green if there be in the vat too large a proportion of sulphate of iron.

When a green ground is wished for upon cloth, acetate of alumina is printed on, and a reserve is applied to the parts that are to remain white, or to those already covered with alumina, which are to take only a yellow colour. The piece is dyed blue, washed with great care to remove all the reserve, and then dyed in weld. It often happens, that the parts of the design which should remain white, take colour in the welding, because the salts of copper and the pipeclay, which constitute the reserve, enter into combination with the cloth. It might be first dyed yellow, but it then becomes impossible to restore the reserve exactly. When there is but little white in the design, the reserve is applied with the pencil.

If with yellow, green, and blue colours, others produced by madder are to be mixed, these should be finished before giving the blue dye.

When the objects to be dyed green are small, or of an irre-



gular form, like leaves or flowers, the blue is put on with the pencil, after finishing all the colours. The green is often made on common cloths, by applying the blue over the rust-yellow, or this over the blue. Thus a sombre green, inclining to yellowish-green, is formed, which is seldom evenly. The difficulty with which the two colours combine prevents this method, otherwise economical, from being employed for dyeing cotton in hanks.

Cotton, which has received a blue with prussian blue, may be dyed green, according to the process described in Sect. II. Chap. V. of the Second Part. The piece, while still moist with the blue, is alumed,\* and passed through a bath of weld, of greater or less strength, according to the shade. Weld causes a livelier colour than old fustic, which deepens more, but deadens a little the vivacity of the blue. If a green, inclining to olive, be wanted, yellow wood (fustic) is preferable. It is dried in the open air, as for blue.

We have described in the same place, the process by which a beautiful blue may be obtained from the combination of prussiate of iron with the stuff. This process applied to cotton, previously dyed olive, by means of alumina and oxyde of iron used as mordants, and a yellow colouring substance, affords a more beautiful green than what can be procured by any other method. In this operation, the iron combines with the prussic acid, forming blue, while the alumina constitutes a yellow with the colouring substance. Bancroft was correct in combating the explanation given of this formation of green, in which the co-operation of alumina was not introduced.†

This green, which resists well the action of light and air, is destroyed by alkalies; and the observations made on blue must be applied to it.

The green obtained by giving a yellow colour to a stuff which has been previously dyed blue, and afterwards washed, presents nothing obscure. The colour inclines more or less to yellow, or to blue, according to the tint of blue given, and the strength of the yellow bath. The intensity of the yellow is increased by alkalies, by sulphate of lime, by ammoniacal salts. It is diminished by acids, alum, and solution of tin. The shades

\* *L'art du fabriquant de velours de coton.*

† *Annal. de chim. tom. xiii.*

vary likewise from the nature of the yellow substance employed.

These different effects will be obtained with the same ingredients in the formation of the Saxon green, according to the process adopted. If the Saxon blue be first dyed, and the yellow colour be next given separately, the effects will be analogous to those just mentioned; but, if solution of indigo be mixed with the yellow ingredients, the results are not the same, because the sulphuric acid acts in this case on the colouring particles, impairing the intensity of the yellow.

It has been formerly remarked, that the sulphuric acid retained by the stuff in the Saxon blue, produced this effect always to a small extent; which makes fustic be preferred to other articles for this species of dyeing.

When a *suite* of shades is to be dyed in a bath composed of yellow and solution of indigo, the latter incline more and more to yellow, because the molecules of the indigo attach themselves to the stuff, in preference to the yellow, which thereby becomes predominant in the bath.

Although the sulphate of copper, and even the verdigris, sometimes used, principally for dyeing linen and cotton, possess in themselves a blue colour, they give, however, to the stuff a greenish shade, because the oxyde of copper which fixes on it, assumes this colour in several circumstances, and particularly when exposed to the atmosphere. This colour is changed to an olive hue, by means of a yellow substance.

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## CHAPTER II.

### *Of the Mixture of Red and Blue.*

FROM this mixture are obtained violet, purple (columbine), dove-colour, pansy, amaranth, lilac, mallow, and a great many other shades, determined by the nature of the substances whose red colour is combined with a blue colour, of which one becomes more or less predominant over the other, according to the proportions of the ingredients, and the other circumstances of the process.

Stuff dyed scarlet, takes, according to the observations of Hellot, an unequal colour, when blue is to be united with it. It is proper, therefore, to begin with the blue ground, which, even for violet and purple, ought not to be deeper than the shade denominated sky-blue. A *bouillon* is given with alum, mixed with two-fifths of tartar; the stuff is next passed through a bath composed of nearly two-thirds as much cochineal as for scarlet, to which tartar is always added. The purple process is distinguished from the violet one, because, for the first, a lighter blue ground is given, and a somewhat greater proportion of cochineal is employed. These colours are often dyed in the sequel of the *reddening* bath of scarlet, by adding the quantities of cochineal and tartar deemed necessary. The operation is conducted in the same manner as for scarlet.

Lilacs, pigeon-necks, mallows, &c., are passed usually through the *bouillon* that has served for violet, with the addition of alum and tartar. The blue ground is proportioned to the shade wanted, as well as the quantity of cochineal. For some reddish shades, as peach-blossom, a little solution of tin is added. It may be remarked, that, although the quantity of cochineal is diminished when a light shade is wished for, yet the quantity of tartar is not; so that its relative proportion to the cochineal is greater, the lighter the colour is to be.

Poerner conceives, that, in order to obtain the colours which result from red and blue, there is an advantage in using solution of indigo in sulphuric acid, because a great variety of shades may more easily be procured, and because the process is not so long or expensive. But the colours thereby obtained are less durable than when the blue vat is employed. He says, however, that they have sufficient permanence, if a solution of indigo be used to which some alkali has been added.

The effects may be easily varied, by giving a preparation to the stuff with different proportions of alum and tartar, or with solution of tin; and by dyeing with different proportions of cochineal and solution of indigo.

In silks, two kinds of violets are distinguished; the fine violet and the spurious. The last is made either with archil or brazil wood.

For fine violet, the cochineal dye is first given, and the vat is then used. The silk is prepared, and receives the cochineal as

for crimson,—with this difference, that neither tartar nor solution of tin, which serve to heighten the colour, is put into the bath. More or less cochineal is introduced, according to the intensity of the shade that is wanted. The ordinary dose for a fine violet is an eighth of cochineal to one of silk. When the silk is dyed, it is washed, with two beetlings, in the river; it is next passed through a vat of greater or less strength, according to the depth which the violet is to have; and lastly, it is washed and dried with the precautions proper for all colours that are dyed in the vat. In order to give more strength and beauty to the violet, it is usually passed through the archil bath; and this practice, frequently abused, is indispensable for the light shades, because the colour would otherwise be too dull.

When silk has been dyed with cochineal, as above directed, a very light shade of blue must be given it for purple. Only the deepest shades are passed through a weak vat. For those which are less so, cold water is had recourse to, into which a little of the blue vat is put, because they would take too much blue in the vat itself, however weak it may be. The light shades of this colour, such as pink, gridelin, and peach-blossom, are made in the same manner, with a diminution of the proportion of cochineal.

The spurious violets are given to silk in various ways. The most beautiful, and those most in use, are prepared with archil. The strength of the archil bath is proportioned to the colour wished for: the silk, to which a beetling in the river has been given on its coming out of the soap, is turned through it round the skein sticks. When the colour is thought to be deep enough, a trial is made on a pattern in the vat, to see if it takes the violet that is wanted. If it is found to be at the proper pitch, a beetling is given to the silk at the river, and it is passed through the vat as for fine violets. Less blue, or less archil, is given, according as the violet is wished to incline to red or to blue.

Beautiful violets may be produced on silk by means of solution of indigo; but they have little permanence, and become reddish, because the colour of indigo fades first.

A violet is made on silk by passing it through water in which verdigris has been dissolved, instead of the aluming; after which a bath of logwood is given. It here takes a blue colour,

which is converted into violet, either by adding alum to the bath, or by passing it through a solution more or less charged with alum, which serves to give a red colour to the particles of the logwood. It is needless to observe, that this violet is very fugitive, and of but moderate beauty. One is made possessing more beauty, and to which much intensity can be given, by passing the alumed silk through a bath of brazil wood, and, after washing it in the river, through a bath of archil.

Madder also is had recourse to for dyeing cloth after giving it a blue ground. By this means are obtained *couleur du roi*, *minime*, and dull amaranth. Nut-galls are usually joined to the madder, and for light shades brazil wood. A browning to a greater or less degree is given to the deep shades with solution of sulphate of iron. These colours are more beautiful when kermes, and particularly cochineal, are mixed with the madder.

By employing solution of indigo with madder, in the same way as with cochineal, brown colours may be formed, according to Poerner, which incline more to red the less solution of indigo is employed. Alum and tartar may serve for the preparation, but alum should not be put into the bath.

Poerner employs brazil wood, and solution of indigo, for obtaining different colours, which incline more or less to blue and red, by a process similar to that pointed out for cochineal and madder. These colours are beautiful; but it is needless to expect durable colours by this method. The ingredients which procure the greatest fixity to them are sulphate of lime, sulphate of zinc (white vitriol), acetate of copper (crystals of verdigris), which must be added to the bath.

Logwood is, moreover, had recourse to for obtaining sloe, damascene, purple, as well as other shades. This wood, joined to nut-galls, communicates all these colours with much facility to wool previously dyed blue. When it is wished to brown them, they are let down again with a little sulphate of iron, by which means shades are obtained which are more difficult to hit by more durable ingredients, but they have little permanence. Fast colours, which have been much esteemed, have, however, been obtained from logwood and fernambucca. To Descroizilles, who is engaged in the arts with the intelligence of a skilful chemist, we owe the following details on the process employed, of which incorrect descriptions have been given.

"Giros de Gentilly," wrote he to the author of the former edition, "is the first who gave success in France to the durable dye with violet wood fixed by solution of tin. He made the first trials at Louviers with MM. Petou (the nephew) and Frigard, about twelve years ago. From what he suffered to transpire concerning the ingredients of his mordant, I succeeded in a tolerable imitation. I made a solution of tin in sulphuric acid, then added muriate of soda, red acidulous tartarate of potash, and sulphate of copper. My success was sufficiently great to induce Giros to propose a partnership with me in the very lucrative business which he carried on at Louviers, Elbeuf, Abbeville, Sedan, and in the Pays de Liege. Giros then taught me a much more convenient method of effecting this combination. It consists in making a solution of tin in a mixture of sulphuric acid, muriate of soda, and water. To this solution the tartarate and the sulphate were added in powder. We made no less than 375 gallons of this mordant in 24 hours, in a single vessel of lead moderately heated. We continued this very profitable trade at the rate of 15 pence per pound for three years, after which it went on declining, till we lost it altogether. The following was the cause of this: Giros having allowed his secret to transpire, we had imitators, who made it at first worse, afterwards better, than we did. In a composition so complex as this, in an operation so obscure as the fixation of colouring matters, it is almost impossible to attain perfection otherwise than by groping our way (*tatonnements*) amid trials which may be indefinitely varied by the respective doses, and especially by the *modus agendi*; and this much more than could at first be imagined by chemists who have not been so long occupied with this object as myself. I do not blush, therefore, to acknowledge, that I was forced to abandon this trade, whilst I saw, and still see, persons who are in no respect chemists deriving a creditable profit from it. What led me to give it up entirely was the invention of the new process of bleaching goods, to whose improvement I have almost entirely devoted myself.

"After thus giving you the history of the mordant of the *prune de monsieur*, I present you with the following account of its employment and effects:—

"If it be wool in the fleece which is to be dyed, one-third

of its weight of mordant is required; if it be a woven stuff, only a fifth is necessary. A bath is prepared at a temperature which the hand can bear; the mordant is well mixed with it; and the wool or stuff is then immersed. It is to be properly agitated, and the same degree of heat is to be kept up for two hours, which may be even increased a little towards the end. It is then lifted out, aired, and very well washed. A new bath of pure water at the same heat is prepared; a sufficient quantity of violet wood is added to it; the stuff is then let down, and agitated; and the heat is urged to the boiling point, at which it is maintained for a quarter of an hour. The stuff is then lifted out, aired, and carefully rinsed. The dye is now completed. If a decoction of one pound of logwood has been used for three pounds of wool, (and proportionately for the stuffs which require a smaller dose,) a beautiful violet is obtained, to which a sufficient quantity of brazil wood gives the shade known by the name of *prune de monsieur*.

“The colouring matters susceptible of being fixed with advantage on wool by this mordant are those of violet and red woods, as also the wood of fustet. Yellow wood (fustic) affords likewise tolerable colours. The colours thus given by the violet and red woods may be afterwards affected by soap or urine in the fulling; and this change, always produced by alkaline substances, may be remedied by a bath very slightly acid, and a little more than lukewarm, called the brightening (*avivage*.) Sulphuric acid is preferred. The colour comes out as deep, and often more brilliant than before this alteration. Wools dyed with this mordant are capable of being spun into more beautiful and finer thread than when alum has been used. By omitting the sulphate of copper, we obtain from fustet and fustic, as well as from weld, more beautiful colours. Madder gives in this case a red-orange colour, but not so deep as with an equal dose of alum. The omission of the sulphate of copper renders the wools much harsher; and besides, the mordant so prepared affords only paltry colours with logwood, and particularly with red wood. One of the great defects of this mordant, before it had been improved, was, and occasionally still is, to make the colours unevenly; whenever they are uniform, they are very beautiful, very harmless, and very soft. This process succeeds equally well on silk. By substituting acetate of lead for sulphate of

copper, it succeeds tolerably well with cotton and linen yarn previously galled. The employment and carriage of this mordant are inconvenient, on account of the dense deposite, which half fills the vessel under a corrosive liquid, which can be kept only in hard stoneware. I possess, however, a method of obviating these inconveniences, by omitting entirely the water in the receipt; by which means I have merely a kind of paste, of a much more commodious employment, and two-fifths cheaper in the carriage. Now that the muriate of soda is low-priced, it may happen that I shall recommence furnishing our dyers with this mordant, which is better, in my opinion, than what they are at present getting, and especially much cheaper. But before doing so, I must devote myself for some time, still, to the composition and employment of your *lixivium*."

For fixing on silk the colour of brazil and logwood, Fabroni has given a process which we shall copy from Hermstadt. It has a good deal of resemblance to that of Descroizilles. It consists in employing as a mordant, a mixture of muriate of tin, sulphate of copper and tartar. Infusion of nut-galls or alderwood bark is added to the bath. The proportions of these substances are varied according to the shade that is wanted. For light shades, a little muriatic acid is added.

When the sulphuric solution of indigo is employed, the sulphuric acid acts differently according to the red substance that is used. It changes very little the colour of cochineal, which had, indeed, a tendency to take a crimson colour by the preparation with alum; but it must give a dun colour to madder, on which the acids readily produce this effect; and it is improbable that this substance could be successfully employed in this process. It would be better to have recourse to it for dyeing stuff to which a blue ground had been previously given. Brazil wood and logwood must also be ill qualified to afford beautiful colours with the sulphuric solution of indigo, because the acids make them turn yellow, although in a less decided manner; but they retain, as we have already remarked, their red colour, when their colouring particles are precipitated by oxyde of tin.

If we may venture an opinion, without having made direct experiments on a complicated process, such as that communicated by Descroizilles, and which is still employed advantage-



ously in some manufactories with modifications which we do not know, we would suggest the following explanation.

The muriate of soda is decomposed by the sulphuric acid, and the muriatic acid set at liberty dissolves the tin.

A portion of the tin is precipitated by the tartaric acid, whence the deposit is occasioned. But a portion which remains in solution serves to modify the effect, as we have seen with regard to cochineal. The oxyde of copper present in this preparation, forms blue with the colouring particles of the indigo; the oxyde of tin with the same wood gives violet, and red with the colouring matter of brazil wood. Descroizilles observed, that a preparation capable of accomplishing this object could easily be obtained, by trying different mixtures, and different proportions, with the muriate of tin: this is what Fabroni has done.

This direct mixture of the blue and red colours gives to cotton yarn and cloth only a sombre hue without lustre, approaching to black, provided these colours be somewhat deep. But if, after giving a light blue to cotton stuff, we dye it of a rose colour with carthamus, a brilliant deep blue is produced, which fades pretty quickly, from the little permanence of the colour of carthamus.

Chaptal has, however, obtained a tolerably agreeable violet, by dyeing red cottons blue, in the preparation of which he diminished the quantities of oils and nut-galls, and, on the other hand, increased that of alum, as well as the brightening process. He attempted, by a great many experiments, to give cotton a violet colour, which would yield neither in durability nor in lustre to the red made in his dyehouses; and after having been led by his researches to a great variety of processes, which afforded with more or less facility the colour which he wished, he preferred the following, as being the simplest and most certain in the execution.

The mordant for 220 pounds of cotton, is prepared with 55 pounds of sulphate of iron, and 13 pounds of acetate of lead. The clear liquid is to be separated from the deposit that is formed; and the cotton is passed through it with the greatest care, after receiving three oils, as for the Adrianople red, as hot as possible. On taking it out of the bath, it is wrung and well

worked: whenever it has assumed, on cooling, the buff shade, it is well washed, wrung out, and dried with accurate stretching.

Its own weight of madder is employed for dyeing: as soon as the bath becomes tepid, the cotton is plunged in, and turned about, with gradual increase of the heat, but without boiling. When the cotton has become blueish-black, it is taken out, and washed. It is thereafter brightened in soap, during fifteen or twenty minutes.

For deep violet, he takes cotton which has received only two oils; he passes it through the same mordant with the same care. He adds a pailful of blood to the madder bath, and takes out the cotton when it is about to boil, washes it, and madders a second time with double its weight of madder, and a pailful of blood. He lets the bath boil for a quarter of an hour; and after washing the cotton, he brightens it with 88 pounds of soap, causing the brightening process to boil for a quarter of an hour, and sometimes more than an hour, as he perceives the colour to be impoverished, or to take lustre.

By adding 11 pounds of alum to the preceding mordant, the violet is more brilliant. He used with advantage the solution of iron in pyrolignous acid.

For procuring uniform colours which penetrate thoroughly, he recommends us to employ the mordant very limpid, and as hot as possible; to wash it on taking it out of the mordant; to dry quickly and equally; but not to let the madder bath boil, when it is wished to preserve the lustre of the dye. Lastly, he observes, that soda makes the colour turn red, and that soap gives predominance to the blue; hence, by employing different proportions of these substances, the shades of the cotton may be varied in the brightening, and blackish cottons may, for instance, be restored to violet by using leys only, whilst if they incline to red, soap alone ought to be used.

To produce violets on printed calicoes, the acetate of iron diluted with water is impressed, and they are maddered. This colour is less easily degraded in the dyeing bath than the reds. It may also be kept boiling for a longer time, so as to raise the deep shades. The bath becomes very foul; the colour comes out of it very dull, and assumes lustre only by exposure on the grass, and ebullition with bran water; it is even rare for the

white to become beautiful again. But these inconveniences are obviated by dunging with a strong heat, which acts less upon this mordant than upon that employed for the reds.

For lilac, a mordant is printed on, composed of very dilute acetate of iron, mixed with a small quantity of acetate of alumina.

Cotton in hanks dyed by the same processes, with difficulty takes an agreeable shade; and the colour never has the permanence of that produced by the processes of Chaptal. The most ordinary method of dyeing linen yarn and cotton violet, consists in giving first a blue ground in the vat, proportioned to the shade wanted, and then to dry it. It is next galled at the rate of 3 parts of nut-galls for 16 parts of the matter; it is left for twelve or fifteen hours in the bath of galls; after which it is wrung out, and dried. The linen yarn and cotton are thereafter passed through a decoction of logwood, and when it is well soaked, it is lifted out, and there are added to this bath 1-60th of alum, and 1-128th of verdigris, both in solution. The hanks passed over the sticks are re-immersed, and they are turned round them for a full quarter of an hour. They are now taken out to let them be aired; they are then replunged completely into the bath for a quarter of an hour; after which they are lifted out and wrung. Lastly, the vat which has served for this dye is emptied; there is poured into it one-half of the decoction of logwood, which was reserved; as much alum is added as in the first operation; and the yarn is once more passed through, till it be of the suitable shade. The decoction of logwood should be more or less rich, according to the depth of shade wanted. This violet resists the air tolerably well, but it cannot be compared in durability to the dyes above described, or even to the following:—

The cotton or linen yarn is scoured as usual; a mordant is prepared, composed of seven pints of acetate of iron, and nearly two gallons of water for every two pounds. This is boiled, and the scum which rises is removed. When no more froth appears, the liquor is poured into a vat, and whenever it is merely tepid, 4½ ounces of sulphate of copper, and about an ounce of saltpetre, are dissolved in it. After this, the hanks are allowed to soak in it during ten or twelve hours, when they are wrung out and dried. When it is wished to madder them, they are

washed with care, and passed through a madder bath. If the violet is to be deep, two ounces of verdigris are added to the mordant. The colour may be still further deepened by galling the yarn more or less before passing it through the mordant, and by leaving out the saltpetre. If the dose of the latter substance be increased, and that of the sulphate of copper be diminished, the violet inclines more towards the lilac. The mordants may be still modified in different manners, so as to produce a great many shades.

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### CHAPTER III.

#### *Of the mixture of Red and Yellow.*

IN treating of cochineal, we thought it improper to separate the operations which usually succeed one another in the dye-houses, and therefore the principal shades obtainable by the mixture of the red of cochineal with yellow have been already described. The shades may receive an infinity of modifications from the different proportions of the ingredients; from the yellow substances made choice of, from the preparations given to the cloth, and from the mordants added to the dye-baths. Thus Poerner describes a great many varieties which he obtained by employing weld, saw-wort, dyers'-broom, and some other yellow substances; as also by introducing into the preparation of the cloth, or into the bath, tartar, alum, sulphate of zinc, or sulphate of copper.

Different colours may in like manner be procured from the madder which is associated with yellow substances. It is thus that the chocolates and the cinnamons are dyed; colours commonly formed in two baths. The maddering is first given, preceded by a *bouillon* of alum and tartar as for ordinary maddering; and then a bath of weld is employed.

For cinnamon a weaker maddering is given, and commonly a bath is used which had served for the chocolate. The proportions are varied according as the red or the yellow is wished to predominate. Sometimes nut-galls are added, and sometimes the colour is deepened by a browning.

Occasionally the sole object is to give a reddish tone to the yellow; the stuff just dyed yellow may, in this case, be passed through a bath of madder, more or less charged according to the intention.

Brazil wood is likewise employed along with the yellow substances, and sometimes it is associated with cochineal and madder.

When, instead of weld or other yellow substances, root of walnut, walnut peels, or sumach, are used, tobacco, snuff, chestnut, musk colours, &c. are produced.

The chestnuts, the cinnamons, and all the intermediate shades, are formed upon silk by means of logwood, brazil wood, and fustet.

The silk is boiled as usual, then alumed, and a bath is prepared by mixing the decoctions of the above three woods, which have been separately made. The proportion of each is varied according to the desired shade; that of fustet ought, however, to predominate. The bath should be of a moderate temperature. The silk is turned round the skein sticks, and when its colour is uniform, it is wrung out, and passed through a second bath of the three ingredients, so proportioned to the effect of the first bath as to obtain the shade wanted.

The mixture of red and yellow requires no peculiar observations in addition to those which have been detailed in the two preceding chapters.

For some colours, blue is blended with red and yellow; thus olives are made. A blue ground is given, then the yellow bath is used, and lastly, a slight maddering is employed. The shade resulting from this operation depends on the proportion of the three colours of which it is composed; for the deep shades, a browning is given with a stronger or weaker solution of sulphate of iron.

The blue vat is not used for producing the olives on silk; but after the aluming, the silk is passed through a very strong bath of weld: some logwood is then added to this bath, and whenever the silk is turned through it, a little alkaline solution is poured in, which turns it green, and makes the cloth take an olive hue. The silk is passed again through this bath, till it has taken the proper shade. For the colour termed *russet olive*, or *rotten olive*, fustet and logwood, without alkali, are added to the bath after

the welding. If a more reddish colour be wished for, only logwood is added. A kind of reddish olive is also made by dyeing the silk in a bath of fustet, to which more or less sulphate of iron and logwood are added.

According to Le Pileur d'Apligny, a fine olive is formed on linen yarn and cotton, by boiling, in a sufficient quantity of water, four parts of weld with one of potash; brazil wood, soaked the evening before, is boiled apart with a little verdigris: the two solutions are mixed in different proportions, according to the shades wanted, and the thread or cotton is passed through the mixture.

The colours which result from the mixture of yellow with red, as *coquelicot*, (poppy-red,) brick, capuchin, &c., are obtained in calico printing by means of weld and madder. Acetate of alumina is printed on as the mordant; and a slight maddering, with a welding finish, is given.

To vary the shades, it is sufficient to increase or diminish the duration of one of the two dyeing operations, or the proportion of the materials employed. These processes are applicable to the dyeing of cotton in hanks, (cotton yarns.)

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## CHAPTER IV.

### *Of the Colours resulting from the mixture of Black with other Colours, and of Brownings.*

THE processes by which the degradations of black are obtained that form the different shades of grey, have been already described. It has been shown, that dissimilar (*étrangères*) shades might be blended with them, so as to cause them to incline towards certain colours; but the black is often employed for certain colours which are to remain predominant, and which should be merely browned. At the same time they become more durable. In the course of this work it has been frequently stated that a browning was imparted to certain colours; but this chapter is destined to treat peculiarly of this operation, and of the resources which it presents to the art, sometimes for the imitat-

ing colours that can be obtained by other means, and sometimes for producing new colours.

To give a browning, the stuff just dyed is passed through a solution of sulphate of iron with which an astringent is mixed, and which consequently forms a *black bath*. More frequently there is added to a water bath a small quantity of solution of iron; and just so much is introduced as to make the dyed stuff attain the wished-for shade. More rarely, some sulphate of iron is added to the dyeing bath. But the desired effect is obtained with more precision by passing the coloured stuff through solution of sulphate of iron. Poerner often macerates the stuff in a solution of sulphate of iron, to which other ingredients are sometimes added; and on its quitting this mordant, he passes it through a dyeing bath.

The first method is employed for chestnuts, coffees, damascenes, and other brown shades of the common dye; greater or less depth of colour is given, according to the colour wished to be obtained by the browning; a bath is next made with nutgalls, sumach, and alder bark, to which sulphate of iron is added. The stuffs which are to be lightest coloured are first passed through; and when they are finished, those that are to be browned are dipped, adding at each operation a quantity of sulphate of iron proportioned to the purpose in view.

The other brownings offer nothing peculiar in the operation. We shall select some examples of the effects that are obtained, and point out some particular processes.

It has been stated in the *first Section* of this *Second Part*, that for several kinds of grey a slight blue ground is given. Poerner makes blueish-greys by employing sulphuric solution of indigo, which he adds to a decoction of gall-nuts with sulphate of iron; and he varies the shades by the different proportions of these three ingredients. He procures other shades by adding sulphate of iron to a bath composed of cochineal, fustic, and gall-nuts.

For *couleur du roi*, a sky-blue ground is given with pastel; the dyeing is performed with weld and a sixth of gall-nuts, and a browning is imparted with the solution of sulphate of iron.

Chestnut, and the colours approaching it, are made with sandal-wood, gall-nuts, and a browning; sometimes fernam-

bucca (brazil-wood) is added. To these colours a cast of purple and crimson is given, by dyeing them in the remains of a cochineal bath, with the addition of a little madder and cochineal to the bath. The colour is rendered lighter by means of a little tartar.

For the hazel colours, gall-nuts, fustic, and logwood are blended, to which more or less madder, and a little alum, are added.

Logwood and brazil wood, being employed in equal parts, or in other proportions, afford different brown colours of tolerable durability, when more or less solution of iron is mixed with their decoction, and when the wool, previously alumed and galled, is dyed in it. These colours cannot be compared, however, with the preceding, in respect to permanence.

To the above colours, different shades of mordorés and capucine may be given, by passing them through a bath of annotto on their coming out of the dye.

A great variety of shades are obtained by the mixture of brazil-wood, logwood, archil, gall-nuts, and by browning with sulphate of iron; but these shades are all more or less fugitive, although they possess an alluring lustre.

When a stuff which has received a colour is passed through a black bath more or less dilute, the effect obtained is simple; a black shade, more or less deep, is blended with the first colour.

This is not the case when the coloured stuff is passed through a solution of sulphate of iron: here the colouring particles that are fixed on the stuff act on the sulphate of iron, seize a portion of its oxyde, combining it with them and with the stuff. The colour that results from this combination is more or less deep, not according to the colour peculiar to the colouring particles, but principally according to the action which they exercise on the metallic oxyde, agreeably to the principles laid down in the *First Part*. Thus the brazil wood and logwood, which enter into the composition of a colour, will produce a much more marked effect in the browning than madder and cochineal; nut-galls and sumach will occasion a still more considerable one, although they had affected the primitive colour only by a dun-coloured shade.

If a black bath be prepared, or a black dye be formed,



either in the mordant, or in the dyeing bath, the ingredients which are mixed with the colouring substances modify the result of the operation, by the action which they exercise on the black molecules: thus alum, solution of tin, solution of indigo, will impair the effect that the black molecules would have produced. All the acids act in the same way, excepting acetic acid, and some analogous vegetable acids, which do not possess the property of dissolving the black molecules. It appears that nitre can dissolve them, since it renders the colours for which it is employed lighter.

As the best colours that can be given to linen and cotton are derived from madder, attention must be paid to the methods described, in treating of madder, for rendering this dye more durable, and its colour may be deepened by different black baths.

For some hazels and snuff-colours, a browning is given, after the welding and the madder bath, with soot, to which gall-nuts and fustic are joined. Soot is sometimes mixed with this bath, and a browning is moreover given with solution of sulphate of iron.

Walnut peels are occasionally substituted for solutions of iron, in browning colours. They have a great advantage for the wools intended for tapestry. The colour does not become yellow by long exposure to the air, as happens to the brownings from iron; but it keeps long without alteration. It has, indeed, a dull tone, suitable for shadows, and for representing the flesh in old figures, which would produce merely gloomy colours, without lustre, on cloths. The goodness of this colour, however, and its cheapness, ought to extend its use for the sombre colours which are sometimes in fashion, at least on common stuffs.

A great number of shades are made at the Gobelins by means of this browning. To procure an assortment of them, a *bouillon* is first given to the woollen yarns with tartar and alum, of different degrees of strength, according to the shades required; they are then successively dyed red, yellow, or some other colour, recurring to the bath from which most effect is wished to be obtained. When the colour is found to be of the desired shade, it is passed, for a shorter or longer time, through the bath of walnut peels, of a strength adjusted to its purpose. This browning is likewise had recourse to for silk; but the

bath must be hardly tepid, in order to avoid the inequalities to which it is so liable.

For the different shades of chestnut, the cotton is galled, passed with the ordinary manipulation through water into which a greater or less quantity of acetate of iron has been poured. It is next worked in a bath in which verdigris has been dissolved; and a welding is given it. It is dyed in a bath of fustic, to which solution of soda and alum are sometimes added. When the cotton which has received these preparations has been well washed, a good maddering is given it. It is then passed through a weak solution of sulphate of copper, and lastly through soap water.

The cinnamon and chocolate colours are given to linen and cotton, by commencing the dyeing with verdigris and weld; they are next passed through a solution of sulphate of iron, which is called the security bath, (*bain d'assurance*), and they are wrung out and dried. When dry they are galled in the proportion of two ounces of gall-nuts per pound; they are once more dried, alumed as for red, and maddered. When they are dyed and washed, they are passed through very hot soap water, in which they are turned round the sticks till they are sufficiently brightened. Decoction of fustic is sometimes added to the aluming.

By taking cotton which had received the requisite preparations for the Adrianople red, and had been galled, then passing it through nitrate of iron, galling it anew and aluming, Chaptal obtained a pretty *nacarat*. He prepares the nitrate of iron with the aquafortis of commerce, diluted with half its weight of water, into which he plunges fragments of iron, which he removes whenever he perceives the solution slackening. The liquor is now of a yellowish-red, strongly acid, and marks from 76° to 108° Twaddell.

If, after galling the cotton that has passed through the oils, it be alumed in a bath to which one-eighth of this solution of iron, for one of cotton, is added, the cotton comes out black, and takes a violet sloe colour by the maddering and brightening.

Chaptal obtains a succession of shades by passing the cotton, which has received two or three oils, through a mordant composed of alum, sulphate of iron, and acetate of lead, and by

varying the proportion of the salts which enter into its composition. Thus, with three parts of alum, two of acetate of lead, and one of sulphate of iron, maddering twice, and brightening with 55 pounds of soap, he produces a sloe colour, inclining towards red. He had, on the other hand, a sloe verging towards violet, by galling with nut-galls and sumach, passing through a mordant prepared with 4 ounces of sulphate of iron, 4 ounces of alum, 2 ounces of acetate of lead, 1 ounce of muriate of ammonia, and as much soda dissolved in 4 pounds six ounces of water, maddering, passing through a boiling ley which marked  $20^{\circ}$ , and brightening with soap.

He took advantage of the difficulty with which alumed and dried cotton is impregnated with water, for dyeing it at once of two colours, which produce the effect of small *chinures* (veins?) very close together, and very irregular. With this view, after having galled, alumed, and dried the cotton which had been treated with the oils, he washed it and dried it anew; then he passed it slightly through one of the above mordants. The down alone (on the surface) is coloured black, and the thread remains grey: after the maddering and brightening, the latter is red, and the down has assumed a violet colour. Cottons dyed in this manner have a very agreeable appearance. Employed in weaving, they produce cloths whose reflections vary, and take different tints, according to their relative position, and that of the dye.

In the manufacture of printed calicoes, colours are obtained from madder, which result from the mixture of red and black. For mordants, mixtures, in different proportions, of acetate of iron and acetate of alumina, are employed.

By printing on a mordant composed of equal parts of oxydized acetate of iron (*black bouillon*) and acetate of alumina, both concentrated, a deep chocolate is obtained with madder. One part of acetate of iron, and two of acetate of alumina, afford a less sombre chocolate, inclining towards puce-coloured. On augmenting the quantity of acetate of alumina, the shade approaches more and more to red; and on introducing, at last, only 1-12th of acetate of iron, an amaranth colour is obtained. If, on the contrary, the proportion of acetate of iron be increased, browns are produced.

This colour is that which requires most madder. It may be

boiled longer than for the reds, but not so long as for the violets, because, as the portion of the colouring matter which is combined with the alumina does not stand a prolonged ebullition so well as that which has the oxyde of iron for a mordant, the shade is degraded, and there is obtained only a poor and unequal colour, instead of a substantial and well raised one. Great care should also be taken to put into the bath a sufficient quantity of madder, so as to saturate all the mordant; otherwise a uniform colour can never be obtained, for the bath becomes exhausted, and some parts of the cloth would be saturated before other parts had been able to assume the proper shade. For conducting the operation properly, and for completely saturating the mordant, the maddering should be given at two times. The bath is scarcely suffered to boil the first time, and from the hue that the cloth has taken, the quantity of madder to be employed at the second maddering may be determined. When the cloth is to have, besides chocolate, fainter colours, they should not be printed on till after the first maddering, because the heat of the bath in the double maddering would degrade them.

The chocolates have a more agreeable hue, when, previous to maddering, they have been dyed with nearly half the quantity of weld or quercitron which would have been used had they been dyed with these substances alone. The mordants for chocolate and puce afford, with both these substances, the shades of olive, bronze, terre d'Egypte, &c. In this case, it is sufficient for restoring the white, to pass through bran on their quitting the boiler, and to expose them for about eight days on the grass, lifting them once in this interval in order to wash and beetle them. The colour has more lustre when, before drying the cloth, we pass it through water acidulated so slightly with sulphuric acid, as to be hardly perceptible to the taste.

These processes may be employed for dyeing cotton in hanks. The greatest precaution should then be taken to impregnate and dry the cotton very equably; for many difficulties are encountered in preventing some parts from being unequally charged with the one mordant or the other.

**N O T E S,**  
**ILLUSTRATIVE AND SUPPLEMENTARY,**  
**BY THE TRANSLATOR.**



## NOTES.

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### NOTE A. p. 33.

THE green of plants, whose colour Mr. Bertholet regards as simple, is a substance which has been lately examined, under the name of *Chlorophile*, by MM. Pelletier and Caventou. They obtained it by pressing, and then washing in water, the substance of many leaves, and afterwards treating it with alcohol. A matter was dissolved, which, when separated by evaporation, and purified by washing in hot water, appeared as a deep green resinous substance. It dissolves entirely in alcohol, ether, oils, or alkalies; it is not altered by exposure to air; it is softened by heat, but does not melt; it burns with flame, and leaves a bulky coal. Hot water slightly dissolves it. Acetic acid is the only acid that dissolves it in great quantity. If an earthy or metallic salt be mixed with the alcoholic solution, and then alkali or alkaline subcarbonate be added, the oxyde or earth is thrown down in combination with much of the green substance, forming a lake. These lakes appear moderately permanent when exposed to the air. Chlorophile is supposed to be a peculiar proximate principle.

### NOTE B. p. 45.

MESSRS. Thenard and Roard published, in the *Annales de Chimie*, vol. lix., a very interesting memoir on mordants, in which the effects of alum, acetate of alumina, tartar, and the solutions of tin, upon vegetable and animal substances, are examined and analyzed. This memoir is translated into the 39th vol. of *Tilloch's Magazine*.

Prior to their experiments, it had been generally supposed that, in the process of aluming, the alum was decomposed, and that the alumina combined with the stuff, thereby causing it more readily to take the colour when plunged into the dyeing bath; but Messrs. Thenard and Roard came to a different conclusion.

*Analysis of the Aluming of Silk.*

One thousand four hundred and seventy-five grains of silk, well cleaned, and perfectly purified, were infused in a glass vessel during six days, at the common temperature of the atmosphere, with four quarts of distilled water, containing 1550 grains of pure alum, which had been previously dissolved in it. After standing this time, the silk was taken out of the liquid, drained completely over the bath, and washed several times with distilled water, to separate that part of the mordant which had not combined with it. The alum bath and the washings were then evaporated with the greatest care, and they afforded very transparent crystals of alum. These first products indicated pretty clearly the nature of the combination which had been formed with the silk during the steeping, and that the alum had not been decomposed. The alumed silk was then boiled in a matrass with six quarts of distilled water, the boiling liquor was poured off from it; and in this manner it was treated twelve times. The 72 quarts proceeding from these operations being evaporated, we obtained well formed crystals of alum, the quantity of which, added to that obtained from the bath, amounted to about 3 grains of the 1475 grains originally employed, forming a loss of  $\frac{1}{16}$  part only. If after each of the twelve washings we attempt to dye the silk, the colour is less deep in proportion to the number of washings, so that after the twelfth the silk is not at all coloured. If the silk, after having thus been washed, is again impregnated with alum, it reacquires the same property of retaining the colour which it had before the washing commenced. Hence results a very natural explanation of the reason why alumed silks take a deeper colour when the dyeing is commenced at a low temperature, than when they are plunged into boiling baths; it is because, in the one case, the action of the boiling water upon the mordant is so speedy that there is not time for the colouring matter to fix upon it and render the combination insoluble; whilst, in the other case, no such effect takes place.

*Analysis of the Impregnation of Wool with Alum.*

After having thus ascertained the phenomena which take place in the aluming of silk, it was necessary to continue the trials upon wool, and to employ for these experiments only perfectly pure materials, completely deprived of the carbonate of lime, which is generally contained in considerable quantity. To separate the whole of this, we boiled the wool several successive times, in a matrass with weak muriatic acid; but in order to take up the last portions of this acid, we were obliged to make use of such large quantities of distilled water, that we were on the point



of abandoning such tedious experiments, requiring so much time and patience, as well as the greatest care. The separation of all the muriatic acid from the first seven ounces of wool which we purified, required 200 quarts of distilled water, at  $212^{\circ}$  Fahr., divided into twenty successive operations, each occupying from seven to eight hours. When calcined and properly tried, it afforded neither lime nor muriatic acid.

Three ounces and a half of this wool were alumed with the same care which had been taken with the silk. It was afterwards washed twenty times, employing six quarts of distilled water, heated to  $212^{\circ}$ , for each washing. Immediately after the aluming, this wool took a very deep colour, whilst after the last washing, it would not take any more colour in the dyeing bath, than some of the same wool which had never been alumed. These experiments convinced us, that the substance which had been fixed in the wool by aluming, and had caused it to receive so deep a colour in the first dyeing, had now been carried off by the water. The alum bath, when evaporated, afforded us, in the state of crystals, two-thirds of the quantity of alum we had originally employed; very nearly the whole of the remaining third part was obtained from the residue of the bath, in an uncrystallized state, and from the washings of the wool. This experiment was repeated several times, and always with the same result; but as this did not appear to us so decisive as the experiment upon silk, on account of the difficulty of separating the animal matter from the last portions of the alum bath, we alumed some wool in the cold as we had done with the silk, and we obtained from the bath and the washings the alum employed in the operation, with a loss only of  $\frac{1}{10}$  part: we were therefore assured, that in the aluming of all animal substances, the alum combines entirely with them, without undergoing any decomposition, and that it forms with them combinations more or less soluble, which have a great affinity for the colouring matters.

*Analysis of the Impregnation of Cotton and (Linen) Thread with Alum.*

Having freed some cotton, by the methods already mentioned, from all foreign matters, we macerated it for two days in a lukewarm solution of a given quantity of alum. After this operation, the stuff took the dye remarkably well; but being treated with boiling distilled water, it lost the property of taking the colour in the dye bath. The alum bath and washings, when evaporated, afforded us all the alum we had employed. We separated this alum from the vegetable matter which it had dissolved in its different crystallizations. To do this, did not require such a number of washings as were employed for the wool or the silk, because the combination of alum with vegetable substances is so weak, that soaking the

alumed cotton in boiling water for a few minutes, is sufficient to carry off the greatest part of the mordant. Cotton, therefore, ought to be dyed at a low temperature, since it is only after the colouring matter has rendered the combination insoluble, that it can support a great heat without being attacked. Thread treated in the same manner as cotton, afforded us the same results.

*Analysis of the Impregnation of common Wool.*

The analyses we have already related most decidedly demonstrate, that in the aluming of all animal and vegetable substances, the alum combines with them without undergoing any decomposition ; but we thought it was necessary to repeat the same experiments upon these substances, in the state in which they are commonly met with in commerce, as we had done in their purified state. Wool, when impregnated with alum alone, always renders the bath turbid, which, upon cooling, throws down an abundant white precipitate, as has been observed by several chemists. Several analyses of this sediment, after being well washed, have constantly afforded us some sulphate of lime, saturated sulphate of alumina, and sometimes a little alumina. The bath contained a remarkable quantity of alum, of acidulated sulphate of potash, combined with a small proportion of animal matter. Upon the wool we found alum, and a very minute proportion of the precipitate. These experiments upon the sediment formed in the alum bath, do not differ from those made by M. Berthollet ; but this learned chemist not having examined the mother waters, nor the alumed wool, has not given, as he himself says, a clear and precise explanation of the effects produced by alum and tartar in the operation of dyeing. These precipitates, obtained by treating common wool with alum, never take place with purified wool ; and as these only differ from each other by the former containing some carbonate of lime, it was natural in this case to attribute to this substance the decomposition of a part of the alum.

We satisfied ourselves of this, by mixing in glass vessels solutions of alum in boiling water, with different proportions of pure carbonate of lime. We always found the alum was decomposed by the carbonate of lime, and that if a sufficient quantity was added, there remained no part of the aluminous salt in solution. The mother waters contained very acid sulphate of potash, and the sediment was formed of sulphate of lime and acidulate sulphate of alumina and potash ; whence it follows, that the property possessed by common wool, of forming a precipitate in the alum bath, and rendering the fluid very acid, is in reality owing to the carbonate of lime it contains. The same result was obtained by aluming common wool five or six successive times in the same bath. But in order to arrive at a

general solution of this question, it was necessary to ascertain the nature of the precipitates formed in the solution of alum, by different alkaline and earthy substances. We took, therefore, alums with base of potash, and with base of ammonia, which we treated with ammonia and carbonate of potash, so as to leave in the solution but a slight excess of alum. The mother waters evaporated, contained very acid sulphates of ammonia, of potash and ammonia, and of potash, according to the nature of the alum and of the precipitate employed. The sediment, which was acid sulphate of alumina and potash, or ammonia, treated with sulphuric acid, afforded alum and acidulated sulphate of alumina; boiled afterwards a great number of times with distilled water, it was converted into alum, sulphate of potash, and pure alumina. There was always a greater quantity of acidulated sulphate of potash than of alum, even in the last washings.

Solutions of alum, treated at a boiling heat with pure alumina, were converted into a very acid sulphate of potash, and into acidulated sulphate of alumina and potash. These results do not at all correspond with those obtained by M. Vauquelin in his experiments upon the alums of commerce, for we have never been able to obtain the saturated sulphate of alumina and potash, spoken of by that celebrated chemist.

Thus all the alkaline and earthy substances mixed in suitable proportions with solutions of alum, converted that salt into acidulated sulphate of potash or ammonia, and into insoluble acid sulphate of alumina and potash, or ammonia, for which reason we have named it the acidulated sulphate, instead of the saturated sulphate, the name it has borne until now. It is evident, that if too great a quantity of carbonate of lime be employed, and the same holds good with the carbonates of barytes and strontian, we shall only obtain alumina and the sulphates of potash, lime, barytes, or strontian. There remains no doubt, therefore, of the nature of the changes produced in the alum baths by the common wools, and of the prejudicial effects of alkalis in the baths intended for cottons; for the addition of these substances diminishes the quantity of alum, and even increases the acidity of the bath.

*On the Impregnation of Vegetable and Animal Matters with Acetate of Alumina.*

Wool, silk, cotton, and thread, in the different states in which these substances are employed for dyeing, were treated with acetate of alumina, which combined entirely with them. But as in exposing them to the air, or to a temperature a little elevated, the mordant always loses a small quantity of acid, it follows that the combination formed upon the stuff is an acetate with excess of base: thus, by treating it with boiling water

it is converted into acidulated acetate of alumina, which is dissolved, and into alumina which cannot be carried off by the water.

*Of the action of Acidulated Tartrate of Potash on Wool.*

Purified wool was treated, as in the former experiments, with very pure cream of tartar, free from tartrate of lime, and formed directly by the tartaric acid and potash. This wool was washed a great number of times, until the last washing did not contain any of the principles which had been combined with it. The bath afforded, by evaporation, three-fourths of the cream of tartar employed, or rather neutral tartrate of potash. The washings were very acid, and we obtained from them a small quantity of cream of tartar, and a very acid composition, formed of tartaric acid and wool. These facts may be thought sufficient to explain the phenomena which take place in impregnating wool with alum and tartar, since we already know, from the experiments of M. Berthollet, that these two salts are not decomposed; and as we have shown that the wool combines completely with the alum, and that it acts upon the cream of tartar by separating the tartaric acid, with which it unites in the most intimate manner. But in order to have these facts rigorously demonstrated, we repeated this experiment, although a very tedious one, in the method already pointed out in the preceding chapters.

*Of the action of Alum and Tartar upon Wool.*

Before treating the wool with alum and cream of tartar, we made some trials of the reciprocal action of these two salts. We ascertained that water, at the temperature of  $12^{\circ}$  or  $14^{\circ}$  ( $65^{\circ}$  F.), holds in solution only  $\frac{1}{150}$  part of its weight of cream of tartar; that boiling water dissolves  $\frac{1}{10}$  of its weight, and that a mixture of equal parts of alum and cream of tartar dissolves in  $\frac{1}{3}$  the quantity of water required to dissolve the salts separately at the same temperature. These results do not differ from those already obtained by M. Berthollet, who has shown that alum has the property of increasing the solubility of cream of tartar.

If wool is alumed in the ordinary proportions, which are  $\frac{1}{4}$  of the weight of the stuff of alum, and  $\frac{1}{10}$  of cream of tartar, all the substances being perfectly pure, we obtain from the bath, when evaporated, alum, cream of tartar, and a residue difficultly crystallizable, composed of tartrate of potash and an animal matter: the washings of the wool will give alum, a small quantity, scarcely appreciable, of cream of tartar, and a very acid combination, formed of a large quantity of tartaric acid, alum, and animal matter.

These experiments remove all uncertainty concerning many practical facts, which at present are only noticed by the dyer in a vague way, and point out to him the precise method of applying the mordants, according to the nature of the colour he wishes to obtain. Indeed, since by making use of alum and tartar, the wool is impregnated with alum and a large quantity of tartaric acid, these two salts should never be employed together, *except* where the colour is susceptible of being heightened and rendered brighter by acids, as is the case with cochineal, madder, and kermes. On the contrary, alum should never be employed for wools intended to be dyed with woad or brazil wood, the colour of which is easily altered or destroyed by acids. Among all the vegetable and animal substances, we have made choice of wool only for trial with alum, and alum and tartar, because it is only with this substance these mordants are made use of in dyeing.

*On the action of Acids, and of some Salts employed as Mordants upon Wool.*

Although all researches hitherto made have been ineffectual to find a substitute for alum, we have nevertheless made trial of a great number of substances with wool ; less, however, for the purpose of discovering the best mordants, than for determining the action of several substances very soluble, and at the same time endowed with great powers. We boiled wool for two hours in water, in which were put small quantities of sulphuric, nitric, muriatic, and tartaric acids. In each instance, the wool, especially when combined with sulphuric acid, struck with cochineal and madder deeper colours than when impregnated with alum and tartar. No doubt, therefore, can be entertained of their superiority in similar cases ; but of all the mordants we tried, there is not one which gives such bright colours as what are obtained by means of the acid tartrate of alumina, (notwithstanding the opinion of M. Haussman to the contrary.) This salt would, in a great number of cases, be preferable to tartar and alum, if its price was not so much higher than theirs. Whilst we were occupied in inquiring with the greatest care into every thing relative to the nature and mode of combination of mordants with various stuffs, we did not forget to examine the several methods which have been adopted in the workshops for a long time past, in order to ascertain if the proportions of alum and tartar, the most generally employed, were those the most suitable for the purpose ; if the time employed for the alum bath was sufficient properly to impregnate the wool ; and if the exposure to the cool air afterwards, for several days, which is so generally thought necessary, is attended with the expected advantages.

Equal parts of the mordants, that is, half the weight of the stuff, produced no better effect than one-fourth ; but between this quantity and one-twentieth part, the colours of cochineal, kermes, and madder, were weaker in proportion to the diminution of the quantity of the salts ; whilst, on the contrary, the effects were reversed with woad and brazil wood, so that in these last substances the colour was deeper the more the salts were diminished. No difference could be observed in the colour, whether the wools had been in the alum bath for two, four, or six hours ; it is, therefore, useless to continue stuffs in the bath longer than two hours. Our experiments did not discover that there was any difference in the colour, whether the dyeing took place immediately after the aluming, or was protracted for some time, except only that wool impregnated with alum alone, produced a deeper colour with woad, after having been exposed some time to a cool air, which we attributed to the separation of the acidulated sulphate of potash, this being carried off with the uncombined mordant in drying.

#### *Of the Scarlet Colour.*

Scarlet is that bright and shining colour which is produced in wool, by treating it with tartar, cochineal, and a highly oxydized solution of tin. Before the discovery of this method, for which we are entirely indebted to Drebbel, those colours were called scarlet which are produced in woollen stuffs by kermes or cochineal, when alum and tartar were employed as mordants. These processes for obtaining the colour have long been known in the dyeing houses, yet no theoretic investigations have been made into the phenomena which take place when a solution of tin is used with cream of tartar and cochineal. Dr. Bancroft attempted to explain what passes in the formation of this colour ; but as his opinion does not appear to be founded on any experiments, we considered the question as not at all determined by his labours. We propose, therefore, to determine the chemical nature of the combination formed upon wool by cochineal, tartar, and a solution of tin, and to make known the result of our inquiries upon the colour of scarlet.

#### *Examination of the Precipitate formed by the Solution of Tin, and the Bitartrate of Potash.*

All the substances employed by us in our experiments were perfectly pure, and we constantly made use of glass vessels and distilled water. 1240 grains of bitartrate of potash, dissolved in six pints of distilled water, were macerated for two hours, at 212° F. of heat, with 125 grains of a solution of peroxyde of tin. The precipitate, which we obtained was

washed several times, and distilled in a small curved retort, the beak of which being plunged into lime water, there was disengaged a sensible quantity of carbonic acid. Proper re-agents indicated, in other portions of it, the presence of a great deal of tin and muriatic acid. Thus the cream of tartar and solution of tin are decomposed, and produce a precipitate, consisting of tartaric acid, and a great quantity of muriatic acid and tin. The mother water contains tartrate of potash, bitartrate, very acid muriate of tin, and a considerable proportion of precipitate, held in solution by excess of muriatic acid.

Very pure white wool, treated with the ordinary proportions of solution of tin and cream of tartar employed in dyeing scarlet, was washed a great number of times in boiling water, which carried off all the substances combined with it. These washings, collected and evaporated, afforded us the same principles we had before obtained from the precipitate formed by the solution of tin and cream of tartar: we also examined, in the same way, the action of cochineal, and found no difference in the results. From these facts we are, to a certainty, convinced, that the fine scarlet colour is produced by the wool being combined with colouring matter, tartaric acid, muriatic acid, and peroxyde of tin. But we shall mistake, if we think the bath has no influence on the colour; for wool, combined with the mordants we shall presently mention, and dyed with cochineal, never takes the scarlet hue unless some acid be added, which causes the colour to pass from yellowish to red, and at length to a bright colour. This last experiment, and some others which we shall relate towards the close of this memoir, proved to us, that the wool is not coloured yellow by the combination it forms with the nitric acid in excess in the solution of tin, for this wool comes out perfectly white from all the boilings it undergoes with the tin, when no colouring matter is employed.

#### *Of Tartrate of Tin, and some other Metallic Solutions.*

The proofs we have already given of the formation of scarlet, appear to us so decisive, that we should not have thought of increasing the number, had not the importance of the question induced us to extend further our labours on this subject.

We tried upon wool, in the usual proportions for dyeing scarlet, all the sulphates and muriates of antimony, bismuth, zinc, arsenic. Some of these solutions afforded very agreeable colours, but very different from what we were seeking to obtain. We were more fortunate in our attempts with the tartrate of tin, obtained from tartrate of potash and soda, and a highly oxydized muriate of tin. This salt, dissolved in muriatic acid, and used in the operation of dyeing, afforded us a scarlet colour, as beau-

tiful and bright as those obtained by cream of tartar and a solution of tin. The tartrate of tin, also, dissolved in an excess of its own acid, produced very good effects : however, as this method would be more costly than the ordinary processes, it is best to employ the solution of this salt in muriatic acid. But before recommending this mordant to be used in the dye-houses, we intend to make trial of it in the large way, so as to determine precisely the expense of it, and what advantages will be obtained by its employment.

*Experiments on the Colour of Scarlet and the Oxydes of Tin.*

Scarlet, as we have already seen, is obtained by treating wool with determined proportions of cochineal, bitartrate of potash, and a highly oxydized solution of tin. The operation of dyeing is divided into two parts ; the first taking up an hour and a half, the latter half an hour : this division is necessary to produce a good colour, which would be weaker and more yellow if all the substances were mixed in the first operation, and applied to the wool for two hours. This circumstance is owing to the very acid state of the bath, which holds in solution a great part of the mordant and of the colouring matter. We obtain the contrary effect when the mordants only are employed in the first operation, and the cochineal reserved for the second.

Pieces of very beautiful scarlet cloth, macerated in distilled water, at a boiling heat, gave out to the water a portion of their colour, and when the operation was finished, appeared only of a light flesh-colour. The washings, collected and evaporated, were very acid, and contained, besides the colouring substance and animal matter, tartaric acid, muriatic acid, and oxyde of tin. Scarlet, therefore, as we have already shown, is a combination in some measure soluble, which, in parting with a small quantity of acid, changes its shade, and may, by repeated washings at elevated temperatures, and with a large bulk of fluid, be rendered completely colourless.

It results from the experiments related in this memoir,—

1. That in aluming all vegetable and animal substances, it is not the alumina which combines with them, but the entire alum ; and that, when these matters are not purified, the lime which they contain occasions a decomposition of a part of this mordant.
2. That all the alkaline and earthy bases, mixed with a solution of alum, decompose it, and convert it into acid sulphate of potash, and into an insoluble salt, less acid than alum, which may, by repeated washings, be converted into pure alumina, sulphate of potash, and alum.
3. That the acetate of alumina combines also in its entire state with



silk, wool, cotton, and thread; that this compound retains its acid but feebly, and loses a portion of it by simple exposure to the air; and that it is then changed into acid acetate of alumina, which is carried off by water, and into alumina which remains upon the stuffs.

4. That alum and tartar are not decomposed, but that the solubility of the latter is increased by the mixture; and that in impregnating wools either with tartar, or alum and tartar, the tartar alone is decomposed; that the tartaric acid and alum combine with the stuff, and tartrate of potash remains in the bath.

5. That the most powerful acids have the property, when combined with wool, of fixing the colouring matters: a property possessed in a high degree by the acid tartrate of alumina.

6. That alum and tartar cannot be employed indifferently for all colours, and that their proportions must depend upon the nature of the colouring matter; that the time of aluming should not be more than two hours, and that the exposure of the stuffs in a moist place, after the mordants are applied, is of no utility in augmenting the intensity of their colour.

7. That highly oxydized tartrate of tin, dissolved in muriatic acid, may supply the place of cream of tartar and the solution of tin in dyeing scarlet.

8. Lastly, that these experiments furnish some useful hints for combining mordants with the stuffs to be dyed, and for improving several of the processes of dyeing.

To complete these researches relative to the action of mordants, it would without doubt be necessary to determine, in the most accurate manner, the changes produced in these combinations by the colouring matters, when applied to the different stuffs.

#### NOTE C. p. 46.

SOME fraudulent chemical manufacturers take advantage of the analogous properties of oxyde of zinc to that of tin, to prepare a permuriate of tin containing a considerable quantity of zinc, which is only about the sixth of the value of tin. The adulteration is the more complete and secure, inasmuch as the oxyde of zinc dissolves equally as well as the oxyde of tin in an excess of caustic alkali, which is the chief test it has to undergo, as the calico-printer is generally satisfied if the precipitate thrown down by caustic alkali dissolves in an excess. If, however, from the colours obtained, or otherwise, there is reason to suspect the purity of the permuriate of tin solution, a stream of sulphuretted hydrogen should be sent through a small quantity of it until all the tin be

precipitated. If the acid solution from which the tin has been precipitated give a white precipitate when it is neutralized with ammonia and a current of sulphuretted hydrogen sent through it, we may be sure it contains zinc. The above method may be used in estimating the quantity of zinc, using, of course, weighed quantities.

It is, however, only due to the chemical manufacturers to state that they themselves are sometimes deceived. I once had occasion to analyse an alloy of zinc and tin containing one part of the former to two of the latter. This alloy had been sold to a chemical manufacturer as tin, and had been used as such to make solutions of muriate and permuriate, before he was aware of the fraud practised upon him.

#### NOTE D. p. 49.

ACETATE of alumina is now most frequently made for the calico printers, by dissolving alum in a solution of crude acetate of lime, (pyrolignite :) a gallon of the acetate, of specific gravity 1.050, or, 1.060, being used with  $2\frac{1}{2}$  lbs. of alum. A sulphate of lime is formed, which precipitates, while an acetate of alumina, mixed with some alum, floats above. The specific gravity of this liquid is usually about 1.080. The acetate of alumina employed as a mordant for good colours, is made by the calico printers in Lancashire from

100 pounds of alum,	
75     ,,	acetate of lead,
40 gallons	water.

The alum is dissolved in the water, and when the solution is at from  $150^{\circ}$  to  $170^{\circ}$  Fahr., the acetate of lead is added. The whole, after being properly stirred, is allowed to settle. The mordant is now decanted from the sulphate of lead, and laid aside for use. With these proportions there is not enough of acetate of lead to decompose all the sulphate of alumina in the alum ; but the results of a great many experiments warrant me in saying that these proportions are the best, and that the mordant containing an excess of alum is not only as rich, but that it gives a much brighter colour than one in which the alum is completely decomposed. I am aware that it is generally supposed by chemists, that all the alumina is useless which does not exist as acetate in the mordant. This, however, is an erroneous opinion, for a mordant made with 75 parts of acetate of lead, is as powerful as one made with 125 parts to 100 parts of alum, although it requires 125 parts to decompose all the sulphate of alumina, and 164 parts acetate of lead, if we wish at the same time to decompose the sulphate of potash of that quantity of alum.

Berthollet recommends the addition of soda and chalk to the alum to saturate its free acid, but printers in general object to the use of either, the soda doing no good, and the chalk positive harm, by the resulting sulphate of lime, which is partially soluble, acting as a mordant, to the prejudice of the colours.

## NOTE E. p. 50.

SEE the figure and description of the padding or blotching machine, in the Appendix.

The action of cow-dung in the process of calico printing, has not been hitherto completely analyzed. It probably seizes that portion of the mordant which is not intimately combined with the cloth, thus depriving it of the power of applying to the rest of the surface, when diffused through the water of the cleansing bath. Thus some animal principle in the dung, by neutralizing the excess of mordant, and possibly precipitating it in an insoluble or inert state, protects the unmordanted spaces from being stained or coloured.

## NOTE F. p. 51.

SEE the figure, and explanation of the wash wheels, at the end of the volume. This mode of washing is by much the most economical and effective. Several other mechanical modes of washing are used in the linen trade.

## NOTE G. p. 51.

BRAN acts in some peculiar way on the colouring matter, but scarcely on the mordants. It seems to loosen and remove the colouring matter; as also to alter its hue in some cases, an effect obvious in the bran pinks.

## NOTE H. p. 51.

THE strength of the solution of chloride of lime for clearing calico grounds, varies according to the goodness of the white to be cleared, and the capability of the colour to bear it. From half a pound to a pound of the dry commercial chloride, for 100 gallons of water at 180° Fahrenheit, may be considered as an average proportion.

## NOTE I. p. 53.

JAMES THOMSON, Esq., of Primrose Hill, obtained, in the years 1813 and 1815, two patents for certain improvements in calico printing. His processes, which are very elegant, have since been extensively and advantageously employed. The following is an outline of his specifications. That for 1813 is thus stated:—

First, Mix or combine with the acid called oxymuriatic acid (or dephlo-

gisticated acid of sea salt) and water, some of the alkaline salts or earths hereinafter named, which shall weaken or suspend the power of the said acid in such proportion, that it shall not, in such mixed or combined state, of itself, and without any farther operation, be able to remove the turkey red colour from the cloth, or materially to impair it, within the moderate space of time taken up in the performance of the process hereinafter described.

Secondly, Print, stamp, pencil, or otherwise apply to those parts of the said cloth, which are intended to be either wholly, or in a greater or less degree, deprived of their red colour, some other acid or metallic oxyde, or calx, which has a greater affinity or attraction for the alkaline salt or earth with which the oxymuriatic acid is mixed or combined, than that acid itself possesses: and if any one of the stronger or more powerful acids be employed, which is either of a corrosive nature, and cannot be safely used, or of a volatile nature, and cannot be used conveniently, such acid must be combined with alkalies, earths, metals, or metallic oxydes or calces, so as to form neutral salts, acid salts, or metallic salts, which shall not be too corrosive or too volatile; and such alkalies, earths, metals, or metallic oxydes, or calces only, must be employed, as have a weaker affinity or attraction for the same acid than that acid has for the alkaline salt or earth with which the oxymuriatic acid has been mixed or combined.

Thirdly, After the said acids, oxydes, neutral salts, acid salts, or metallic salts, so directed to be printed, stamped, pencilled, or otherwise applied to the cloth as aforesaid, are sufficiently dry, immerse the cloth in the solution of the said oxymuriatic acid, so mixed or combined with some of the alkaline salts or earths hereinafter named as aforesaid. When the acid or oxyde, either in its simple or combined state, has been applied to parts of the cloth, it immediately seizes upon and combines with the alkaline salt or earth with which the oxymuriatic acid has been mixed or combined, and disengages that acid, which almost instantaneously deprives of their colour those parts of the cloth to which the said acids or oxydes, in their simple or combined state, have been so printed, stamped, pencilled, or otherwise applied as aforesaid.

Lastly, Wash or otherwise remove all the said acids, oxydes, or salts, by the usual processes. For the more fully explaining and illustrating the invention hereinbefore described, I add the following remarks:—The alkaline salts or earths which I mix or combine with the oxymuriatic acid, in order to suspend or prevent its action on those parts of the red cloth which are intended to retain their colour, are the alkaline salts of potash and soda, or the calcareous, magnesian, barytic, or strontitic earths, of which I prefer the calcareous earth.

The acids which I apply to the parts intended to be made white, or to

those places on the cloth intended to be deprived of their red colour, in a greater or less degree, are any of the vegetable, mineral, or animal acids, which have a stronger attraction for the alkaline salt or earth with which the oxymuriatic acid has been mixed or combined, than that acid itself has; such, for instance, are the citric, oxalic, tartaric, malic, benzoic, sulphuric, sulphurous, phosphoric, fluoric, boracic, nitric, muriatic, arsenic, tungstic, succinic, and carbonic acids.

The stronger acids, or such as might corrode the cloth, I saturate more or less with some alkaline salt, earth, or metallic oxyde or calx, for which they have a weaker affinity or attraction than they have for the alkali or earth with which I have combined the oxymuriatic acid: for instance, I unite the sulphuric acid with potash, so as to form the acid sulphate of potash, (or acid vitriolated tartar,) or with aluminous earth, to form alum. The muriatic acid I combine with tin, or copper, or zinc, forming muriate of tin, muriate of copper, or muriate of zinc. In like manner, the nitric acid may be combined with the aluminous earth, or with the volatile alkali, or with the metals, or oxydes of copper, or zinc, or iron, or mercury; and I take care, when I use acidulous compounds of such corrosive acids, not to suffer the acid so far to predominate as to render the compound injurious. In like manner, I combine the volatile acids, or such as might evaporate too speedily, with some alkaline salt or earth, or metallic oxyde or calx, for which they have a weaker affinity or attraction than they have for the alkali or earth with which I have combined the oxymuriatic acid: for instance, I combine the acetic acid with the earth of alum, so as to form acetate of alumina,—or with copper, forming acetate of copper,—or with zinc, forming acetate of zinc. The carbonic acid may also be fixed and combined with an alkali, as with soda, for example, forming carbonate of soda, which may be used, though with less advantage than the preceding combinations. Those acids which are not corrosive nor volatile, and which consequently are used with most advantage in their simple or combined state, may, however, be united, like the preceding, to the alkalies, earths, metals, or metallic oxydes or calces, for which they have a weaker affinity or attraction than they have for the alkali or earth with which the oxymuriatic acid has been united. Thus the tartaric acid may be combined with potash, to form cream of tartar,—and the oxalic acid with potash, to form salt of sorrel,—and these two salts may be employed in the process, though it is not necessary so to combine the two acids; but, on the contrary, the acids may be used alone.

The combinations which I prefer as uniting the greatest number of advantages upon the whole, are, the super-sulphate of potash, (or acid vitriolated tartar,) the sulphate of copper or blue vitriol, the muriate of tin, or sal jovi, the nitrate of copper, and the muriate of copper. But I

prefer to any single combination a mixture of the supersulphate of potash, with the tartaric or citric acids.

Lastly, I employ, uncombined, such metallic oxydes or calces as approach in their properties to the nature of acids, and are capable of combining either with the alkaline salts of potash or soda, or with the calcareous, magnesian, or strontitic earths, or of disengaging them, or any of them, from their combination with oxymuriatic acid : such, for instance, is the oxyde of arsenic, or common white arsenic, and the oxydes of tin and tungsten.

It is evident, from what I have set forth in the preceding part of this specification, that this process admits of great variety in its application, according to the combinations I make use of ; since, not only the various acids, oxydes, and salts I have enumerated, may be employed, but, also various mixtures of them, and in various proportions ; but I prefer and generally use the following process :—

First, I take one gallon of good vinegar, or rectified pyrolignous acid, which I thicken with starch or flour in the way practised by calico printers, in preparing the mordants or colours for printing. Whilst boiling hot, I add to it five pounds of crystallized tartaric acid, and incorporate the whole very well by stirring.

Or, I take one gallon of strong concentrated lime-juice or lemon-juice, or one gallon of water, in which I have dissolved two pounds and a half of crystallized citric acid, which I thicken with starch or flour in the manner directed above, and to which, whilst hot, I add two pounds of supersulphate of potash, and incorporate the whole very well by stirring. I prefer starch to any other thickening, though others may be used with more or less advantage.

Secondly, The paste so prepared I print, stamp, pencil, or otherwise apply to the cloth previously dyed turkey red, in the mode and with the precautions generally used in the printing or stamping of linens or cottons.

Thirdly, I prepare a solution of oxymuriate of lime, either by dissolving the dry oxymuriate of lime (commonly called bleaching powder, or bleaching salts) in water, or by passing the oxymuriatic acid gas into a vat, vessel, or cistern, in which, by agitation or otherwise, I keep suspended such quantity of quicklime as will more than saturate fully and completely the said oxymuriatic acid gas. In either way, I obtain a solution of oxymuriate of lime, with excess of lime. That which I use and prefer is of the specific gravity 1050, and I seldom employ it lower than 1030, (water being considered as 1000.) The vat, vessel, or cistern, which contains the solution of oxymuriate of lime, in which I immerse the cloths, may be of any size or form best adapted to the purpose or situation. I use and prefer vessels of stone of from six to eight feet deep, six to

seven feet long, and three and a half to four feet broad ; but larger or smaller vessels will answer very well.

Fourthly, When the cloths are ready for immersion, which they are as soon as the paste is dry, I hook them on a frame, such as is used in dyeing indigo or china blues, commonly called a dipping frame, on which the cloth should be so disposed that no two folds can touch each other. I then plunge the frame with the cloth so attached into the vat containing the solution of oxymuriate of lime, and keep it gently in motion during the time of immersion, which should not be prolonged more than ten minutes, and which rarely need exceed five minutes. The object being either wholly or partially to remove the turkey red dye from certain parts or places, as soon as that is done the cloth should be withdrawn from the solution of the oxymuriate of lime, and plunged or rinsed in clean water. I practise and approve the aforesaid plan of immersion ; but any other plan or plans by which the cloth can be exposed a greater or less time to the action of the oxymuriate of lime, without bringing one part of the said cloth into contact with another, will answer very well.

Lastly, After having, as before directed, rinsed or washed the cloths in clean water, I free them from all remains of the different agents or substances employed, by the ordinary means of washing, branning, or soaping, as practised by calico printers ; and if those parts of the cloth that are intended to be made white should still retain any red, or other tinge or stain injurious to the effect, in order to render the white complete, I clear it by the usual process of exposure to the air, or by passing the cloth through hot water, to which I have added as much of the solution of oxymuriate of lime as will remove the said stains or tinge, without material injury to those parts from which the red dye is not intended to be removed.

I then proceed, if other colours are to be applied, to finish the cloths by the ordinary and well known methods of calico printers ; but these not being necessarily connected with, nor forming any part of the peculiar process or invention herein intended to be described, I purposely make no mention of here.

The above particulars and examples are given for the more full explanation of the said invention, and the manner in which the same is to be performed. But the invention, whereof I claim the sole and exclusive use, consists in printing, stamping, pencilling, or otherwise applying to those parts of the cloth which are intended to be either wholly, or in a greater or less degree, deprived of their red colour, an acid, oxyde, neutral salt, acid salt, or metallic salt, such as is hereinbefore for that purpose directed, and immersing the whole cloth in such mixture or combination

of oxymuriatic acid and water, with some of the alkaline salts or earths, as is herein directed for that purpose.

Mr. Thomson's patent for 1815, is specified as follows :—

The ordinary practice of calico printers is to apply, with the block or pencil, what are termed after-colours, to certain spaces, originally left in their patterns, and intended to receive the said after-colours ; or to certain spaces on the cloth, from which parts of the original pattern have been discharged, in order to admit, by a subsequent operation, the application of the said after-colours. Now the object of my invention is, by one application of the block, cylinder, roller, plate, pencil, or other mode, to remove parts of the original pattern or colour from the cloth, and at the same time to deposit a metallic oxyde, or earthy base, which shall of itself be a colour, or shall serve as a mordant to some colour to be produced, as hereinafter described.

First, Mix or combine with the acid called oxymuriatic acid (or dephlogisticated acid of sea salt) and water, the alkaline salts of potash or soda, or, which is still better, calcareous earth or quicklime, in such proportion as will weaken or suspend the power of the said acid, so that it shall not in such mixed or combined state, of itself, and without any further operation, be able to remove, or materially to improve the colours, within the moderate space of time taken up in the performance of the process.

Secondly, Print, stamp, pencil, or otherwise apply to those parts of the cloth which are intended to be deprived of one colour and to receive another, a solution of some earthy or metallic salt ; the acid of which having a greater affinity or attraction for the alkaline salt or earth with which the oxymuriatic acid is mixed or combined than that acid itself possesses, will disengage it, and the metallic or earthy base of which being deposited in the cloth, will either of itself be a colour, or serve as a mordant to some other colour, to be produced as hereinafter described.

Thirdly, After the metallic or earthy solution aforesaid has been printed, stamped, pencilled, or otherwise applied to the cloth, as before directed, and is sufficiently dry, immerse the cloth in the solution of oxymuriatic acid, combined with the alkaline salt of potash or soda, or, which I greatly prefer, with calcareous earth or lime, when the acid of the metallic or earthy solution which has been applied to parts of the cloth, will immediately seize upon and combine with the alkaline salt or earth with which the oxymuriatic acid has been mixed or combined, and disengage that acid, which will almost instantaneously deprive of their colour those parts of the cloth to which the said earthy or metallic salt has been applied.

Fourthly, Wash or otherwise remove the said acids or salts by the usual processes, and when the earthy or metallic base, deposited in the cloth, is



intended to receive another colour, proceed to raise it by the usual operations of dyeing, as will be further illustrated in the examples hereafter given of particular applications of this invention. The earthy solutions which I apply to the parts intended to be deprived of their colour, and to receive another, are the solutions of alumina, or earth of alum in acids; such, for example, as the sulphate of alumina, or common alum, the acetate of alumina, or the nitrate or muriate of alumina. The metallic solutions which I employ are, the sulphate of iron or copperas; the nitrate, or muriate, or acetate of iron; the muriate of tin, or nitro-muriate of tin; the sulphate of copper or blue vitriol, or the nitrate, muriate, or acetate of copper. All acids that form soluble compounds with the before-named metals, or the earth of alum, may be employed; but those only which form the most soluble compounds, such, for example, as those enumerated above, can be employed with advantage. For the more full and complete understanding of the principle laid down in the preceding part of this specification, I subjoin the following practical illustration of its application to various kinds of work. If I desire to have a yellow figure or stripe on the cloth, upon which a madder-red ground or pattern has been printed, after having, by the ordinary processes of calico printing, produced the red ground or pattern, I first print, stamp, pencil, or otherwise apply to those parts intended to be yellow, a strong aluminous mordant, composed of three pounds of sugar of lead, and six pounds of alum, dissolved in a gallon of water, and thickened with a due proportion of calcined starch, in the manner usually practised by calico printers.

Secondly, I prepare a solution of oxymuriate of lime, either by dissolving the dry oxymuriate of lime (commonly called bleaching powder, or bleaching salts) in water, or by passing the oxymuriatic gas into a vat, vessel, or cistern, in which, by agitation or otherwise, I keep suspended such quantity of quicklime as will more than saturate fully and completely the said oxymuriatic gas. In either way, I obtain a solution of oxymuriate of lime, with excess of lime. That which I use and prefer is of the specific gravity 1050, and I seldom employ it lower than 1030 (water being considered as 1000.) The vat, vessel, or cistern, which contains the solution of oxymuriate of lime in which I immerse the cloth, may be of any size or form best adapted to the purpose or situation. I use and prefer vessels of stone, of from six to eight feet deep, six to seven feet long, and three and a half to four feet broad; but larger or smaller vessels will answer very well.

Thirdly, When the cloth is ready for immersion, which it is as soon as the paste is dry, I hook it on a frame, such as is used in dyeing indigo or china blues, commonly called a dipping frame, on which the cloth should be so disposed that no two folds can touch each other. I then plunge the frame, with the cloth so attached, into the vat containing the solution of

oxymuriate of lime, and keep it gently in motion during the time of immersion, which rarely need exceed five minutes. The object being to remove the red dye from certain parts or places, as soon as that is done the cloth should be withdrawn from the solution of the oxymuriate of lime, and plunged into or rinsed in cold water. I practise and approve the aforesaid plan of immersion; but any other plan, or plans, by which the cloth can be exposed a greater or less time to the action of the oxymuriate of lime, without bringing one part of the said cloth into contact with another, will answer very well.

Lastly, After having, as before directed, rinsed or washed the cloth in clean water, I free it from all superfluous remains of the different substances employed, by the ordinary means of washing, dinging, and cleaning, as practised by calico printers; after which I dye the cloth and raise the yellow in the usual way, with quercitron bark, or any other yellow dye.

If, instead of yellow, it is proposed to have a buff pattern or figure, I add to the aluminous mordant, prepared and thickened as above, one-fourth or one-sixth, or some intermediate proportion, of a solution of nitrate of iron, and proceed to print and immerse in oxymuriate of lime, as in the former case.

The red dye will be removed as before, and its place be occupied by a buff. If the buff be raised in quercitron bark, an olive will be obtained. By printing at separate times, and on different parts of the cloth, each of the above-mentioned mordants, both yellow and olive figures on a red ground may be obtained. Similar effects, with trifling variations, take place, when, instead of red grounds, purple or chocolate grounds are employed; but it must be observed, that these colours being produced from mordants consisting wholly, or in part, of solutions of iron, and the oxyde of that metal not being removable by the process detailed in this specification, the after-colours produced will be modified more or less by the said oxyde of iron. The foregoing examples are given for the more full explanation of the said invention, and the manner in which the same is to be performed; but the invention, whereof I claim the sole and exclusive use, consists in printing, stamping, pencilling, or otherwise applying to cloth, previously printed and dyed, or dyed any other colour than turkey red, any of the earthy or metallic solutions hereinbefore for that purpose directed, and immersing the whole cloth in such mixture or combination of oxymuriatic acid and water, with some of the alkaline salts or earth, as is herein directed for that purpose, so as to remove the colour or pattern from the part so printed, stamped, pencilled, or receiving such application, and by the same process, fix on such parts either a new colour or a mordant for a new colour.

## NOTE K. p. 114.

JAMES LEE, Esq., of Merton Abbey Flax-Mills, obtained a patent, in 1812, for preparing hemp and flax without the process of steeping and dew-retting. He maintains, that, when the hemp or flax plants are ripe, the farmer has nothing more to do than to pull them, as heretofore practised; to spread and dry them in the sun, as he would his hay or grain, taking care only in the ridges to lay the roots in one direction, so as to prevent as much as possible the breaking or entanglement of the stems; and when sufficiently dry, to carry and lay them in store, either in ricks or barns. No preparation of a canal and running water; no loss of time; no hinderance from harvest, or other business, is necessary. Mr. Lee seems not to have been happy in what relates to the machinery for breaking and manufacturing the flax and hemp prepared by his dry method. For an account of his mechanical contrivances, see some excellent papers on the manufacture of hemp and flax, by John Mittington, Esq., inserted in the Quarterly Journal of Science, Literature, and the Arts, vol. iv. p. 321; vol. v. p. 32; vol. vi. p. 141.

## NOTE L. p. 120.

In a foot-note to page 38, I have adverted briefly to the mode of action by which chlorine destroys vegetable colours. Sir H. Davy first showed that dry chlorine does not bleach dry litmus paper, but that when moisture intervenes the discoloration immediately takes place. When vegetable colouring matter, which consists of hydrogen, oxygen, carbon, and occasionally azote, (as in indigo,) is placed in contact with chlorine and water, the elements react on one another; the greater part of the chlorine seizes the hydrogen to form muriatic acid, while some of it probably unites with the carbon, hydrogen, and azote of the colouring matter, so as to constitute a peculiar compound. The oxygen liberated from the water combines with the carbon, rendering it soluble in alkaline leys. The yellow-coloured substance resulting from the action of chlorine on moist vegetable colouring matter, has not, I believe, been subjected to any rigid ultimate analysis. Till this be done, the theory of bleaching by chlorine must be regarded as imperfect. Of late years, quicklime has been very extensively and profitably employed by the Lancashire bleachers as an alkaline agent. They boil the unbleached cloth in a milk of lime for some time; then wash, and boil in a very weak solution of soda,

## NOTE M. p. 123.

In the Quarterly Journal of Science and the Arts for July, 1822, I published a paper on the composition and manufacture of chloride of

lime, where the proper proportions of the ingredients employed in its formation are investigated. "When a mixture of sulphuric acid, common salt, and black oxide of manganese are the ingredients used, the absolute proportions are,

1 atom of muriate of soda . . . .	7.50	29.70	100.00
1 atom of peroxyde of manganese . .	6.50	21.78	73.30
2 atoms of oil of vitriol, (1.346 sp. gr.)	12.25	48.52	163.30
	<u>25.25</u>	<u>100.00</u>	<u>336.60</u>

"And the products ought to be,

Chlorine disengaged . . . . .	1 atom, 4.5	17.82
Sulphate of soda . . . . .	1 „ 9.0	35.64
Protosulphate of manganese . . . .	1 „ 9.5	37.62
Water . . . . .	2 „ 2.25	8.92
	<u>25.25</u>	<u>100.00</u>

"These proportions are, however, very different from those employed by many, nay, I believe, by all manufacturers; and they ought to be so, on account of the impurity of their oxide of manganese: yet, making allowance for this, I am afraid that many of them commit great errors in the relative quantities of their materials.

"From the preceding computation, it is evident that one ton of salt, with one ton of the above native (impure) oxide of manganese, properly treated, would yield 0.59 of a ton of chlorine, which would impregnate 1.41 ton of slacked lime, producing two tons of bleaching powder, stronger than the average of the commercial specimens; or, allowing for a little loss, which is unavoidable, would afford two tons of ordinary powder, with a little more slacked lime."

I have lately analyzed two samples of recently made bleaching powder, made by two eminent manufacturers, one in Scotland, the other in England, and found the composition as follows:—

Chlorine . . . . .	18.00	16.7
Lime . . . . .	37.00	31.3
Muriate of lime . . . . .	28.50	29.0
Water . . . . .	<u>16.50</u>	<u>100.0</u>
	100.00	100.0

The above quantity of lime is associated or mixed with the chlorine. The muriate of lime (chloride of calcium) is formed in the process, and is a product very disadvantageous to the manufacturer, since it takes up about one-half of his chlorine unprofitably, and adds a compound to his powder probably injurious to the bleacher. Bleaching powder may be formed which contains no appreciable proportion of the muriate of lime, as I have

shown in the above memoir. By proper management, the manufacturer of chloride of lime might therefore double his useful product at scarcely any additional expense.

I may state that a much surer test of the value of chloride of lime, than its power of decolourizing indigo in sulphuric acid, which cannot be depended on, is to see how much chlorine it contains by its action upon protosulphate of iron. For this purpose, dissolve 50 grains of the chloride of lime in tepid water, and make the solution to fill the alkalimeter. Have 100 grains of sulphate of iron dissolved in a tumbler; add the chloride of lime to the iron solution until it ceases to give prussian blue, with drops of prussiate of potash, on a cheese-plate.

The sulphate of iron (100 grains) always requires 12.81 grains of chlorine, which, of course, is the quantity of chlorine in the measures of chloride of lime used. Let the number of measures of chloride used be  $M$ , and the whole number of the measures of the alkalimeter 100, then,

$M : 12.8 :: 50 : \text{the whole chlorine in 50 grains chloride, twice which is the per cent. of chlorine.}$

NOTE N. p. 126.

For a description of a convenient apparatus for preparing dry chloride of lime, see the Quarterly Journal of Science and the Arts, for July, 1822. In making the solution of chloride of lime or potash, the same arrangement of alembics may be adopted, but the chlorine disengaged must be conducted by lead pipes into large wooden vessels lined with lead, or constructed of masonry, which contain the mixture of lime or potash with water. The contents of this vessel or condenser are kept constantly agitated by means of wooden or iron vanes coated with lead, revolving on a vertical axis.

One of the most convenient modes of ascertaining the amount of real alkali in an alkaline solution or substance, is described by Faraday in his work on chemical manipulation. "Into a tube sealed at one end,  $9\frac{1}{4}$  inches long,  $\frac{3}{4}$  of an inch in diameter, and as cylindrical as possible in its whole length, pour 1000 grains of water, and scratch the place where its surface reaches, and divide the space occupied by the water into 100 equal parts. Opposite to the numbers  $23\frac{1}{2}$ , 49,  $54\frac{1}{2}$ , and 65, draw a line, and at the first write soda, at the second, potash, at the third, carbonate of soda, and at the fourth, carbonate of potash. Then prepare a dilute acid having the specific gravity of 1.127° ( $25\frac{1}{2}$  Tw.) at 60° F., which may be made by mixing one measure of concentrated sulphuric acid with four measures of pure water. This is the standard acid to be used in all the experiments, being of such a strength that, when poured into the tube till it reaches either of the four marks just mentioned, we

shall obtain the exact quantity which is necessary for neutralizing 100 grains of the alkali written opposite to it. If, when the acid reaches the word carb. potash, and when, consequently, we have the exact quantity which will neutralize 100 grains of that carbonate, pure water be added until it reaches 1, or the beginning of the scale, each division of this mixture will neutralize one grain of carbonate of potash. All that is now required in order to ascertain the quantity of real carbonate in any specimen of pearlash, is to dissolve 100 grains of the sample in warm water, filter, and add the dilute acid in successive small quantities, until, by the test of litmus paper, the solution is exactly neutralized. Each division of the mixture indicates a grain of pure carbonate. Soda ash may be tested in the same way, using, of course, its proportion of acid."

This, it will be perceived, gives the amount of alkali only contained in the sample; but it is sometimes necessary to know the amount of each of the foreign salts accompanying the soda ash. These salts are invariably muriate and sulphate of soda. To test the amount of these without the trouble of drying and weighing precipitates, we may use the following methods:—For the muriate of soda, dissolve 58 grains of nitrate of silver for every such quantity of water as will make 100 measures of the alkalimeter, the tube described above: 5 grains of muriate of soda dissolved should just precipitate 25 measures of such a solution. It follows, that, operating upon 20 grains, acidifying with pure nitric acid, heating to about 170° F., and adding so long as a precipitate is obtained, the per-centage of muriate of soda in the sample is given.

To test the amount of sulphate of soda, dissolve 23½ grains of nitrate of lead in every 100 measures: 20 grains of sulphate of soda would precipitate 200 such measures. Using then 20 grains, and halving them, we have the per-centage.

To obtain the whole analysis of a soda ash, take 40 grains, dissolve, filter, and multiply the insoluble matter by 2½, to get the per-centage; neutralize with pure nitric acid at 8° Tw.,\* to get the soda; then halve the solution, after supersaturating with nitric acid, and test with the nitrates of silver and lead, for the muriate and sulphate of soda.

#### NOTE P. p. 132.

SULPHURET of lime, as proposed by Mr. Higgins, was extensively employed for one or two years by the linen bleachers of Ireland. Their goods

\* This acid should, on 100 measures of the alkalimeter being taken, saturate 64.6 grains of carbonate of lime, or 68.25 dried carbonate of soda. Either of these quantities is just equal to 40 grains oxide of sodium. So that the per-centage is obtained by weighing 40 grains of any alkaline solution, and ascertaining how many measures are required to saturate it. For potash, use 61 grains.

were, however, much injured by this article, whether from its injudicious use, or otherwise, I do not know. I have been told, however, that this compound has been recently tried in some establishments with advantage.

NOTE Q. p. 135.

THE form of bucking tub (see plate at the end of the volume) now used in this country, is a simplification of Widmer's. It is found to answer perfectly well.

NOTE R. p. 140.

THE introduction of the wash, dash, or splash wheel, of which a representation is given at the end of the volume, may be regarded as a very great improvement in the cotton manufacture of this country. Its velocity must be nicely regulated. When it is too slow, the pieces of goods merely slide down the inclined planes of the partitions; and if too rapid, they are held stationary at the circumference by the excess of centrifugal force. The proper speed is stated in the explanation of the plate.

NOTE S. p. 150.

MR. WELTER, a practical chemist of deserved celebrity, states that a given quantity of chlorine condensed in lime water destroys the colour of as much test solution of indigo, as if it had been condensed in pure water. Hence, it would appear that only chloride of lime is formed, and no muriate or chlorate, for the two latter salts possess no bleaching power; and had any of the chlorine been transformed into them, the discolouring force would have been proportionally impaired. Yet M. Chenevix, in his memoir on the hyperoxymuriates, or chlorates, obtained chlorates of lime and barytes by transmitting chlorine through solutions of these earths in water. Of these conflicting opinions it is difficult to decide which to adopt. The analogy of solution of potash in its action with chlorine, is certainly favourable to the views of M. Chenevix. If the affinity of chloric acid for the bases be greater than that of acetic acid, then it would be possible to determine this point by pouring vinegar on a determinate quantity of liquid chlorate of lime slightly heated. On M. Welter's theory, nearly the whole bulk of condensed chlorine would be recovered; but on M. Chenevix's there would be a very considerable deficiency, corresponding to the quantity of muriate and chlorate formed. A mixture of chlorate and muriate of lime, or of potash, neither of which has any bleaching power, would yield by heat as much oxygen as a pure chloride of lime, in whose formation a like quantity of chlorine had been expended as in that of the above mixtures. Hence this mode of research, which has been recommended on respectable

authority, is illusory, either for estimating the discolouring power of liquors, or for analyzing these compounds.\*

NOTE U. p. 172.

IN Robertson Buchanan's *Treatise on the Management of Fuel*, some useful directions will be found for applying steam to different processes of dyeing.

NOTE V. p. 192.

THE just explanation of the phenomena which occur in the manufacture of sulphuric acid from the combustion of sulphur along with nitre, was first developed by MM. Clement and Desormes; and Sir H. Davy made some important observations on the subject. An outline of their view of this process is given in my *Dictionary of Chemistry*, article ACID (SULPHURIC.) It is a curious fact, that M. Berthollet was the only chemist of eminence who resisted the mass of evidence adduced by MM. Clement and Desormes in favour of their theory, which constitutes one of the most beautiful specimens of chemical research.

NOTE W. p. 204.

THE reasoning in this paragraph about the union of muriatic acid with oxygen, to form oxymuriatic acid, is quite erroneous, and has been long since refuted by Sir H. Davy. A copious abstract of his experiments and investigations will be found in the article CHLORINE of my *Dictionary of Chemistry*.

NOTE X. p. 205.

It is now known that the dry metallic muriates contain no oxygen, and no muriatic acid, but that they are compounds of chlorine with a metal; hence properly called chlorides. M. Berthollet's highly oxydized muriate (such as corrosive sublimate) contains no oxygen, but is a compound of two proportions of chlorine with one of mercury. M. Chenevix's oxygenated muriates are the chlorates of the present day, being compounds of chloric acid with a metallic oxyde, or with ammonia.

NOTE Y. p. 214.

THIS is a mistake. Acetic acid contains no azote.

\* See latter part of note M.



## NOTE Z. p. 217.

By Klaproth's analysis, the alum ore of Tolfa consists of

Silica	.	.	.	.	.	36.50
Alumina	.	.	.	.	.	19.00
Sulphuric acid	.	.	.	.	.	16.50
Potash	.	.	.	.	.	4.00
Water	.	.	.	.	.	3.00
						<hr/>
						99 00

## NOTE AA. p. 219.

ALUM is composed of

Sulphuric acid	.	.	.	.	.	33.00
Alumina	.	.	.	.	.	11.00
Potash	.	.	.	.	.	10.00
Water	.	.	.	.	.	46.00
						<hr/>
						100.00

The common alum of commerce, the potash-sulphate of alumina, requires about sixteen parts of water, at 60° Fah. to dissolve one of it; but there is another species, the soda-sulphate of alumina, soluble in less than its own weight of water, which on this account may become valuable in some processes of dyeing.

The small quantity of iron which is sufficient to deteriorate alum as a mordant, renders it of consequence to be able to test the alum, especially since it may appear pure enough to the eye when it contains a hurtful, although small quantity of iron. All that is necessary for this purpose is to dissolve a few grains of the alum in hot water, and add a solution of caustic potash, until the white precipitate which is at first formed, entirely disappears. If the alum contain iron, brown flakes will remain in the liquor; if not, the mixture will be colourless, and have no precipitate.

## NOTE BB. p. 224.

A PROCESS in calico printing, of peculiar elegance, with an alkaline solution of alumina, was invented by James Thomson, Esq., of Primrose Hill, near Clithero. Its effect was to produce a fast green, by the mixture of a yellow mordant with the common solution of indigo in caustic potash, through the intervention of orpiment. This, as is obvious, could not be done with any acid solution of alumina. Mr. Thomson first formed a solution of that earthen potash, mixed this with the solution of indigo, and applied the mixture, properly thickened, to the cloth. But as, in the ordinary dunging operation, the alkali would naturally wash away with it the greater part

of the alumina, the goods before being dunged were passed through a solution of sal ammoniac. It is easy to perceive the *rationale* of what takes place. The potash on the cloth combines with the muriatic acid of the sal ammoniac, and as the two substances set free (the alumina and ammonia) have no tendency to combine, the former remains precipitated on the cloth at its points of application.

It obtained currently, but very improperly, the name of Warwick's green, because Dr. Warwick made and sold the solution of aluminated potash to the printers.

NOTE CC. p. 226.

THERE is no proposition better established in chemistry, than that the different oxydes of the same metal are compounds of oxygen and the metal in definite proportions, of which the series is regulated by the proportion in the lowest term of oxydizement. The successive oxydes contain oxygen amounting to two, three, or four multiples of that in the protoxide. M. Berthollet was very unfortunate in adopting the notion of indefinite combination, and scarcely pardonable for resisting with such obstinacy the great body of evidence incompatible with his hypothesis.

NOTE DD. p. 289.

OWING to the length of time necessary to saturate pyroligneous acid with iron, some manufacturers make their acetate of iron by the decomposition of sulphate of iron and acetate of lime. This preparation of iron liquor always contains sulphate of lime, and never affords so good colours as that made directly from acid and iron. It is therefore advisable for the printer to test the method by which his acetate has been prepared, which is very simple; for when double decomposition has been resorted to, a considerable excess of sulphate of iron is used to make the precipitate of sulphate of lime settle down. All, then, that is required as a test, is to add to the acetate of iron a few drops of a solution of acetate of barytes; if there be a precipitate, it is sulphate of barytes, and we may be sure that the iron liquor has been made from acetate of lime, and is consequently bad. Acetate of iron gives no precipitate with acetate of barytes, but it does with acetate of lead, which should not be used as a test; as the precipitate is apt to be mistaken for sulphate of lead.

NOTE EE. p. 233.

BEFORE verdigris is pressed into cakes, it is in the form of light blue acicular crystals of a silky lustre, which, by the action of water, are resolved into a soluble acetate and an insoluble subacetate of copper, the latter being decomposed by the action of cold water, which gradually

changes it into a brown powder; whether it is thus totally resolved into oxyde of copper, or whether it remains a sub-salt, has not been ascertained. Mr. R. Phillips states the composition of the silky blue crystals as follows :—

Acetic acid . . .	28.30	1 atom.
Peroxyde of copper . .	43.25	1 „
Water . . .	28.45	5 „

The green decomposable powder obtained by acting on the silky crystals with water, or the subacetate, consists of 50 acid + 160 peroxyde of copper. There remains in solution a binacetate.

The following is Mr. Phillips's analysis of French and English verdigris.

	French.	English.
Acetic acid . . .	29.3	29.62
Peroxyde of copper . .	43.5	44.25
Water . . .	25.2	25.51
Impurity . . .	2.0	0.62
	<hr/> 100.0	<hr/> 100.00
	<i>Phillips's Annals</i> , No. 21.	

#### NOTE FF. p. 255.

MR. BRACONNOT published in the *Annales de chimie*, vol. lxxxiv., a chemical examination of the husks of walnuts. The juice of the husks, examined by re-agents, exhibited the following effects: It strongly reddened infusion of litmus. Solution of gelatin formed in it a slight precipitate, which he ascribed to tannin. Sulphate of iron gave the juice so deep a green, that it appeared black. No precipitation took place, even on standing some time, in consequence of the free acid found in the mixture, which is capable of imparting a fine grey to wool or silk. Oxalate of ammonia indicated the presence of lime. Nitrate of barytes produced no signs of any sulphate. Nitrate of silver acts on it in a manner well adapted to reveal the presence of the alterable hydrocarburet radical, for it produces a pretty copious precipitate, which quickly becomes coloured, while the silver resumes its metallic lustre from the action of the vegetable substance on the oxygen of the oxyde. The precipitate is then no longer soluble, but in part, in nitric acid, and leaves charcoal as a residuum. Alkalies change the juice to a deep red, and form in it precipitates that contain lime. Acetate of lead occasioned in the juice a whitish, flocculent, very copious precipitate, which dissolved entirely in distilled vinegar. From this precipitate, malic and citric acids were obtained. Subacetate of lead produced a new precipitate with the preceding liquid, and rendered the whole nearly colourless. This sediment yielded malic acid, colouring matter,

and tannin. The magma left after expression of the juice, after having been treated with alcohol, which extracted from it some green resinous matter, was heated with water till it boiled, to free it from the starch and the coloured matter it retained. When thus exhausted, it was digested with dilute nitric acid, which separated some phosphate and oxalate of lime, that had been precipitated from the acid liquor by ammonia. The means employed to separate these two earthy salts, which are very frequently associated in vegetables, are founded on the property which distilled vinegar diluted with water has of dissolving phosphate of lime without sensibly affecting the calcareous oxalate.

Though the husk has a peculiar smell, it afforded nothing remarkable by distillation in a water bath.

The incinerated ashes of the husk yielded potash, carbonate of lime, phosphate of lime, and oxyde of iron.

From the above examination it appears, that the fleshy covering of the walnut contains :—

1st, Starch ; 2nd, An acid and bitter substance, very alterable, which appears to approach to the state of charcoal by the contact of air ; 3rd, Malic and citric acids ; 4th, Tannin ; 5th, Phosphate of lime ; 6th, Oxalate of lime ; 7th, Potash.

NOTE GG. p. 280.

GUATIMALA indigo, treated first with water, then with alcohol, and lastly with muriatic acid, afforded to M. Chevreul (Ann. de chimie, vol. lxi. p. 20,) the following products :—

By water	{	A green matter united to ammonia	}	12
		A little deoxydized indigo		
		Extractive		
		Gum		
By alcohol	{	Green matter	}	30
		Red resin		
		A little indigo		
By muriatic acid	{	Red resin . . . . .	}	6
		Carbonate of lime . . . . .		2
		Red oxyde of iron . . . . .		2
		Alumina . . . . .		3
A residuum	{	Of silica . . . . .	}	3
		Pure indigo . . . . .		45
				100

This process might therefore be adopted in the laboratory, for procuring

indigo nearly pure. But when we wish to obtain this colouring substance exempt from all foreign matters, it is better to employ the following method, which we owe to M. Chevreul. About 8 grains of common indigo, in powder, are to be put into a crucible of platinum or silver, which is to be carefully closed, and placed over ignited charcoal. The indigo sublimes, and attaches itself in crystals to the middle portion of the crucible. Another method is, to take the solution of deoxydized indigo, made with a solution of sulphate of iron and lime, or alkali, to decant the clear solution, and expose it to the air. The indigo speedily absorbs oxygen, and becomes insoluble. When it is separated from the liquid, it must be washed first with dilute muriatic acid, then with water, and lastly with alcohol. M. Roard used in this way muriatic acid and water, for purifying on the great scale the very impure indigos obtained from pastil.

In my paper on the ultimate analysis of vegetable and animal substances, which the Royal Society honoured with a place in their Transactions for 1822, the following are stated as the constituents of 100 parts of indigo: Carbon 71.37, hydrogen 4.38, oxygen 14.25, azote 10. Or, carbon 71.37, water (or its elements) 16, azote 10. But the examination of indigo having been undertaken about the same time by my ingenious friend, Mr. Walter Crum, I relinquished the subject. His paper on indigo, drawn up 1822, and published in the Annals of Philosophy for January, 1823, must be regarded as the most elaborate and accurate analysis yet given of this interesting vegetable product. "For procuring indigo perfectly pure, I used," says he, "the covers of two platina crucibles, nearly three inches in diameter, of such a form, that, when placed with their concave sides inwards, they were about three-eighths of an inch distant in the middle. I placed thinly about the centre of the lower one ten grains of precipitated indigo, not in powder, but in small lumps of about a grain in weight; then, having put on the cover, I applied the flame of a spirit-lamp beneath the indigo. In a short time this substance, partially decomposed, begins to melt, and the purple vapour to be disengaged, which is known by the hissing noise that accompanies it. The heat is continued till this noise nearly ceases, when the lamp is withdrawn, and the apparatus allowed to cool. Then, on removing the cover, the sublimed indigo will be found planted upon its inner surface, with sometimes a few long needles upon the bottom of the apparatus, which are easily removed from the button of coaly matter that remains. In this way I have generally obtained eighteen to twenty per cent. of the indigo employed; a small quantity unavoidably escapes, but I am persuaded that very little more can by any means of this kind, be obtained.

"Those who cannot readily procure precipitated indigo for the purpose of subliming, may find it convenient to combine with my method one lately

given in the *Journal de Pharmacie*, by MM. Le Royer and Dumas. It consists in spreading about 30 grains of common indigo in coarse powder upon an open silver capsule, and applying the heat of a spirit-lamp till all the sublimed indigo is formed upon the surface of the ashes. On repeating this process, I find that ten parts of common indigo yield one of sublimed indigo, which is, however, far from being pure. By resublimation in my apparatus, it is again reduced one-half from the loss of its impurities, and some vapour.

"I shall here describe what else takes place during the sublimation. Ten grains of precipitated indigo, in the apparatus I have described, yielded

1.88 grains of sublimed indigo.  
6.44 grains of cinder remained, and consequently  
1.68 grains of volatile matter escaped.

---

10.00

"Thirteen grains of the same indigo, kept a quarter of an hour at a strong red heat in a small platina crucible, firmly, though not exactly closed, left 7.9 grains of cinder, which is equal to 61 per cent.

"In order to ascertain what gases were evolved during this destruction of the indigo, I introduced 5.28 grains into a small glass tube connected with a mercurial trough. On applying the heat of a spirit-lamp, the vapour of indigo was formed, and condensed in the colder part of the tube, but was at last destroyed by repeated applications of heat. A quantity of water appeared in the tube, and 0.96 cubic inch of gas was found in the receiver. On removing the tube, it was found to have lost in weight 0.71 grains, or 13.5 per cent. of the indigo employed. The water that was formed had a disagreeable burnt ammoniacal smell. I found, on analyzing the gas in the receiver, (making allowance for the common air of the apparatus, and a small portion of gas remaining in the tube,) that it consisted, for 100 of indigo, of

Carbonic acid	2.8
Carburetted hydrogen and carbonic oxyde	0.8
Azote	1.9
The difference between the sum of these and the loss 13.5	
was water, with a little ammonia	8.0
	<hr/> 13.5

*Sublimed Indigo.*

"Indigo sublimes in long flat needles, which readily split, when they are bruised, into four-sided prisms.

" Viewed at a particular angle, they have the most brilliant and intense copper colour ; but when lying in heaps, they have a rich chestnut brown colour, one that would be produced by mixing a very little yellow with a bright but deep reddish purple.

" Besides these needles, this substance is found in the form of plates, much broader than the needles, and extremely thin ; twisted sometimes almost into tubes. These appear to the naked eye perfectly opaque. I was not a little pleased, however, with their unexpected appearance, when seen through the microscope. Viewed obliquely, they appear still opaque, and copper-coloured like the needles ; but when held perpendicularly to the rays of light, they are seen to be transparent, and of a beautiful blue colour, exactly similar to a dilute solution of indigo which has been acted upon by sulphuric acid. Their intensity varies, according to the thickness of the plate, from a blue just distinguishable from white, to one almost black. The bronze colour which these crystals assume when in heaps, is obviously a mixture of the copper colour with this blue.

" The vapour of indigo is transparent, and of a most beautiful reddish violet colour, resembling a good deal the vapour of iodine, but sufficiently distinguished from it by the shade of red. The sublimation takes place at the heat of about 550° Fahrenheit ; for the vapour rises at a heat lower than that of melting lead, and requires more than the melting heat of bismuth. Upon the rough bright surface of the lead, I observed some of the crystals melt while the vapour was rising ; but I have in no other circumstances remarked any thing like fusion, till the substance was decomposed. Hence the melting point of indigo, its point of volatilization, and that at which it is decomposed, are remarkably near each other.

" The specific gravity of sublimed indigo is 1.35.

" These crystals sublime when heated in open vessels, leaving no residue. In close vessels, the vapour is at first reddish-violet, as in the open air : but as the heat advances, it acquires a tinge of scarlet ; and before it is entirely decomposed, becomes deep scarlet, and then orange-coloured : a quantity of charcoal is at the same time deposited.

" *Action of Oils.*—Of the essential oils, oil of turpentine dissolves at its boiling heat as much indigo as gives it the fine violet colour of the vapour of indigo ; but a slight reduction of temperature is sufficient to precipitate the whole of it. The fixed oils and fatty substances, as they may be heated to a higher degree, exert a more powerful action upon indigo. None of them that I have tried act upon it at the heat of boiling water ; but when the heat is increased, they gradually dissolve it, acquiring the colour of its vapour much more deep than oil of turpentine does. If the solution be cooled at this period, the indigo precipitates blue. As the heat is continued, more of the indigo is dissolved ; but the colour of the

solution begins to change ; it gradually inclines to crimson, and has then begun to be destroyed. It is now green when cooled. Heated still more, the solution is of a strong crimson ; then becomes orange ; and at last when entirely decomposed, it is yellow, which colour it retains when cold.

*Determination of the Ultimate Constituents of Indigo.*

Carbon . . . . .	73.22
Azote . . . . .	11.26
Oxygen . . . . .	12.60
Hydrogen . . . . .	2.92
	<hr/>
	100.00

These numbers correspond very nearly to

1 atom of azote . . . . .	1.75 or 10.77	
2 atoms of oxygen . . . . .	2.00	12.31
4 atoms of hydrogen . . . . .	0.50	3.08
16 atoms of carbon . . . . .	12.00	73.84
	<hr/>	<hr/>
	16.25	100.00

“I have also made several analyses of well-dried precipitated indigo ; and allowing for a minute portion of lime which it contained, I got results which agreed perfectly with the analyses of sublimed indigo. I find, too, that both these substances are acted upon in the same manner by other bodies. The different effect of heat depends obviously upon some difference in the mechanical arrangement of their particles.

“I made several attempts to amalgamate sublimed indigo, as well by the process of Dobereiner, as by others which I thought more likely to succeed, but in vain. I could in no case perceive the least alteration in the fluidity of the quicksilver.

*Action of Sulphuric Acid upon Indigo.*

“When indigo is digested in concentrated sulphuric acid, it is well known to suffer a remarkable change, being converted into a peculiar blue substance, entirely different from indigo, with which the Saxon blue is dyed.

“This substance has been so little attended to by chemists, that no one has yet thought of giving it a separate name. I shall venture to propose for it that of *cerulin*, from the colour of its solution.

“The mixture of the blue substance with sulphuric acid is a semifluid which requires a considerable quantity of water to dissolve it. When



potash is added to this solution, previously filtered, a deep blue precipitate is formed. I was surprised, however, when making the experiment, to find the precipitate as plentiful before one-fourth of the acid was saturated, as when the solution was made altogether neutral. To another portion, I added potash previously saturated with sulphuric acid, and found the same precipitate formed as with potash alone.\* I threw the precipitate upon a filter, and washed it with water, in order to examine whether it was the pure colouring matter that had separated. The first washing did not take away much of the precipitate; the next, however, sensibly diminished it; but with the third portion of water it almost wholly disappeared.

"In order to discover the cause of this increased solubility, I made a saturated solution of sulphate of potash in water, and putting into it a little of the blue pulpy substance that remained upon the filter, I agitated it thoroughly. The solution remained altogether colourless. I found the same to be the case when the muriate, the acetate, or any other salt of potash, was employed. Alcohol, also, and ether, refused to dissolve this substance. Put into pure water, however, it immediately dissolved, forming the same deep blue solution that had passed through the filter.

"It seemed then only necessary to dissolve in water some salt of potash, to enable it to wash this substance without dissolving it. I found the acetate to answer extremely well; and this salt possesses the advantage over the muriate or sulphate of not being precipitated by alcohol from a weak solution in water, as they are. It may consequently be afterwards removed by washings with alcohol.

"Such edulcorations with acetate of potash I repeated so often upon a quantity of precipitate, taking it every time off the filter and agitating it well in a phial with the liquid, that not  $\frac{1}{1000}$ th of a grain of the original soluble matter could be left in it. I then washed away the weak solution of acetate of potash as well as possible by means of alcohol, without, however, being able to remove all traces of that salt, although I used the alcohol somewhat dilute. The small quantity that remained could not materially affect the experiments I made upon it.

"A portion of the substance thus prepared, when burnt in a large platina crucible, left a considerable quantity of ashes, slightly reddish coloured, which dissolved almost entirely in water. What remained was

\* That the solution of indigo in sulphuric acid is precipitated by neutral salts, is not a new fact. Berthollet, (*Art of Dyeing*, ii. 277.) says, that the "fixed alkalies saturated with carbonic acid," as well as "alcohol, saturated solutions of alum, sulphate of soda, or other salts containing sulphuric acid," form precipitates in this solution. My experiments show, I think, that the effect does not depend upon the presence of sulphuric acid in the precipitant; that some sulphates have no such effect; and that alcohol does not precipitate the original solution at all.

of a deep red, or rather brown colour, and was principally oxyde of iron. The solution of the ashes was not at all alkaline : it gave a dense white precipitate with muriate of barytes ; a very slight one with oxalate of ammonia ; and with sulphate of alumina large crystals of alum were formed in a few hours. It was sulphate of potash.

" From these facts, I have no hesitation in concluding, that this precipitate is a combination of cerulin with sulphate of potash. That salt forms more than a fourth of its weight. It may, therefore, be called *ceruleo-sulphate of potash*.

" The salts of soda also form precipitates in the solution of cerulin with sulphuric acid, and these are likewise insoluble in solutions of potash or soda, though soluble to a certain extent in pure water. When heated, these ceruleo-sulphates dissolve even in solutions of their salts. On cooling, the greater part falls down again in blackish grains ; a portion, however, remaining in solution. The soda compound is evidently more soluble than that of potash. The washings of the former precipitate, with a cold solution of its acetate, are a little more coloured than those of the potash precipitate, with its acetate of the same strength. This last substance is totally insoluble in water containing one per cent. of acetate of potash, or even a half per cent. after two or threeedulcorations. I have generally employed a solution of two parts dry acetate of soda in a hundred of water ; and any quantity of such a liquid may be used without the quantity of the substance being materially diminished.

" The salts of ammonia likewise form precipitates in the sulphuric solution of cerulin, when not much diluted. The precipitate dissolves readily in hot solutions of ammoniacal salts, and again separates when cold, the whole mass becoming curdy. I believe this substance to be a combination of cerulin with sulphate of ammonia, from the quantity of that salt which I found in it, when as well washed as possible. It is much more soluble, however, than the ceruleo-sulphates of potash and soda, and therefore cannot be washed so freely as these fixed alkaline compounds. Potash and soda and their salts decompose it. It dissolves in great quantity in boiling pure water, and in 40 or 50 parts of cold water. It has the same general properties with the more insoluble compounds.

" A corresponding combination with barytes may be formed by decomposing ceruleo-sulphate of potash by muriate of barytes. The compound formed is extremely insoluble. An abundant blue precipitate is thus formed in solutions of ceruleo-sulphate of potash, containing so little sulphuric acid, that they are not troubled in the slightest degree by a barytic salt, when the cerulin has been previously destroyed by nitric acid.

" Similar compounds may be formed with other bases, whose sulphates

are difficultly soluble in water; but these I have not particularly examined.

"The salts of magnesia have no power of precipitating cerulin from its solution. The whole of the sulphuric acid in the original solution may be saturated with magnesia, without any precipitate being formed.

*Ceruleo-sulphate of Potash.*

"This substance is of so deep a blue, when wet with water, as to appear absolutely black. When dry, it has a shining strong copper-red colour. By transmitted light it is blue. It attracts water from the air with great rapidity. In two hours, a portion which had been dried attracted a tenth of its weight.

"It is soluble to a considerable extent in hot water. Cold water takes up  $\frac{1}{14}$ th of its weight of this substance, and forms a solution so deeply coloured, that when diluted with 20 parts of water in a phial of an inch in diameter, it may just be seen to be transparent. Water in a wine glass containing  $\frac{1}{500.000}$ th of its weight of this substance is distinctly blue coloured.

"The saturated solution is precipitated by spring water, and by every liquid that I have tried, except distilled water. From this it appears, that the mere presence of any foreign substance in pure water greatly diminishes its solubility.

"If the solution be diluted with 20 parts of pure water, it is still precipitated by solutions of the salts of potash and soda, lime, barytes, strontian, lead, and mercury. An addition of sulphuric or muriatic acid does not re-dissolve them. But neither ammonia nor any of its salts precipitate this weak solution. None of the salts of magnesia, zinc, or copper, nor the solutions of alum, sulphate of manganese, permuriate of tin, protosulphate or persulphate of iron, or nitrate of silver, precipitate it. It is not precipitated by any of the acids, by infusion of galls, or by pure gelatin. Alcohol and ether do not precipitate the weak aqueous solution, though they do not dissolve any of the dry substance. Ceruleo-sulphate of potash dissolves readily in concentrated sulphuric acid, but not in concentrated muriatic acid.

"When chloride of tin is mixed with the solution of this substance, its colour is immediately changed to yellow. This yellow product is not very soluble in water; it becomes blue again on the addition of any substance, as a salt of copper, capable of imparting oxygen to it.

"When heat is applied to the blue substance, it does not melt; no purple vapour is given off, and in consequence of its being defended by the saline matter, a strong heat long applied is necessary for its being reduced to ashes.

" When luminous objects, as the sun or moon, or the flame of a candle, are viewed through the blue solution of this substance, of the proper degree of intensity, they appear of a fine rich scarlet colour. It is worthy of remark, that a single drop of nitrate or sulphate of copper, mixed with a quantity of this solution, makes the same objects appear blue through it, although the general appearance of the liquid is not in the least degree altered. Zinc produces the same effect, though not so powerfully. Any acid restores to these mixtures the property of making luminous objects appear red, unless when a large quantity of copper has been added, which makes the liquid itself green.

" Sir H. Davy was the first to discover that a vegetable substance had the power of precipitating in combination with certain neutral salts, which are themselves abundantly soluble in water. The carbonates of potash, soda, and ammonia, and the chlorides of tin and of iron, are among the substances which that philosopher found undecomposed in combination with tannin, in the precipitates formed by these salts in an infusion of galls. It appears that cerulin acts a similar part, at least with the sulphuric salts. I am not aware, however, that any substance has been hitherto described by chemists which possesses the property I have found in the one here treated of, that of dissolving in pure water, and refusing to do so in neutral saline solutions which produce no change upon it. But in common life, some idea of this singular fact seems to have been long acted upon. Those who are in the habit of washing printed gowns, particularly dark ones, of colours not very permanent, always rinse them in a solution of common salt, or at least in very hard water, before they hang them up to dry. The salt, they say, fixes the colour, and prevents it from spreading out into the white, which it always does when they are suffered to dry in a cool place, without such immersion.

*On the Phenomena which are exhibited during the Formation of Cerulin.*

" Some of the phenomena which attend the action of sulphuric acid upon indigo, have been noticed by different chemists. Bergmann, in 1776, observed, that when indigo in powder was sprinkled upon sulphuric acid, greenish clouds were produced, which became blue by the addition of a drop of water. He added, that the same effect was produced, but more slowly, without water. Hausmann, of Colmar, observed, that the acid in contact with indigo became at first greenish-yellow, then deep green, and at last blue. That gentleman remarked also, that the ' effervescence and disengagement of sulphurous vapours, always observed in making the blue compound, leave no room to doubt that the acid exerts an action upon the particles of indigo, and that we should be wrong in considering this as a mere solution of indigo unaltered.' Berthollet, in his excellent work on

dyeing, considers the change that takes place a species of combustion ; the sulphuric acid furnishing the indigo with oxygen, and thereby being converted into sulphurous acid. Dr. Bancroft, whose work appeared soon after that of Berthollet, conceived the solution to be oxygenated indigo combined with sulphuric acid. Hence he gave it the name of sulphate of indigo.

“ Such, as far as my information goes, is the extent of our knowledge, or rather our opinions, upon this subject. I shall state what appearances I have myself observed during this process.

“ When indigo is put into sulphuric acid, it is dissolved, and the acid assumes a yellow colour. When this solution is dropped into water, it becomes instantly blue ; but the substance so produced is by no means the same as that which is-formed after some time, without the assistance of water. It is indigo altogether unchanged, which precipitates, and leaves the sulphuric acid perfectly colourless. If the yellow solution be exposed to the open air in a watch-glass for a short time, the blue colour is restored in the same manner, and the indigo falls down. This effect is produced, not by the action of the air, but merely by the absorption of moisture.

“ A considerable increase of heat takes place when the two substances are put together. There can be little doubt that this is caused by the sulphuric acid abstracting and combining with the 14.2 per cent. of water contained in the indigo.

“ If the yellow solution above mentioned be allowed to remain without dilution, it becomes blue in a few hours ; and this is effected without the assistance of air, as I found by making the experiment in a small phial, the mouth of which was sealed up as soon as the materials were put together. In consequence of the darkness of the liquid, these changes of colour can only be observed in the thin film which wets the empty part of the phial, when it is agitated.

“ All the chemists who have treated of this process, mention the formation of sulphurous acid during the solution of indigo, and, attributing this to the action of the indigo itself upon the acid, they naturally concluded that that substance became oxydated at the expense of the acid. But these chemists employed only the indigo of commerce in their experiments ; a substance which contains more than half its weight of impurities, and great part of these vegetable matter. I have found that it is these impurities alone which decompose the acid ; for during the solution of sublimed indigo not a trace of sulphurous acid can be detected, though the heat of boiling water be applied for hours. Neither is there any production of hyposulphuric acid ; for, if there were, it would be decomposed by the heat to which the liquid was exposed, or even by the presence alone of concentrated sulphuric acid, in which case sulphurous acid gas would be given off.

" In less than twenty-four hours, if a slight degree of heat be applied, the indigo is entirely converted into cerulin ; and, when mixed with water, it passes through the filter, leaving no residue whatever.

*On the Constitution of Cerulin.*

" Since there is no production of sulphurous acid, nor absorption of air, during the formation of cerulin, it is clear that there can be no oxydation either of the carbon or hydrogen previously existing in the indigo. No carbon being deposited, and no gas evolved, during this process, prove also that the azote exists in the new substance, in the same proportion to the carbon that it does in indigo. That sulphuric acid does not enter into its composition is evident from its precipitating with almost any sulphuric salt, and carrying down no additional sulphuric acid of its own. It is only in the amount of combined water, then, that any alteration can possibly have taken place ; and to ascertain whether in this case there has been an abstraction or an addition of water to the indigo, it were only necessary to convert a given weight of that substance into cerulin, and to weigh the product, as M. de Saussure has done in the case of starch sugar. There are difficulties, however, which prevent such an experiment from being performed with any precision ; principally the large quantity of sulphuric acid necessarily mixed with the product, and the solubility of the substance in water. I have contented myself with analyzing, by means of peroxide of copper, the ceruleo-sulphate of potash, after having ascertained as nearly as possible, by incineration, how much saline matter it contained. But as this cannot be done with absolute precision, owing to the dissipation of a small portion of acid along with the vegetable matter, my results, particularly with regard to the hydrogen, were by no means so uniform as those which I obtained when operating upon indigo. All that is really necessary in this case, is to determine the quantity of carbon, which may be done with very little risk of error. The deficiency, after adding to the carbon the proportion of azote, and of free hydrogen found in indigo, is water.

" The ultimate composition of the substance is :

Carbon	.	.	.	.	57.18
Azote	.	.	.	.	8.79
Oxygen	.	.	.	.	29.32
Hydrogen	.	.	.	.	4.71
					<hr/>
					100.00

This approaches so near to *indigo* + 4 *water*, that there can be little doubt such is its constitution.

1 atom azote . . .	1.75 or 8.43	
6 atoms oxygen . . .	6.00	28.92
8 atoms hydrogen . . .	1.00	4.82
16 atoms carbon . . .	12.00	57.83
	<hr/>	<hr/>
	20.75	100.00

" There is not the slightest proof that any combination exists between cerulin and sulphuric acid in the original liquid. Alkalies, it is true, precipitate it from the solution ; and this has been supposed to be the effect of a superior attraction on the part of the acid for the alkali, by which the vegetable substance was left at liberty ; but such a theory falls to the ground as soon as it becomes known that neutral salts produce exactly the same effect ; that magnesia does not precipitate it at all, though it neutralizes the acid ; and that cerulin is itself soluble in water. Cerulin dissolves, indeed, in sulphuric acid, and that more abundantly than in water ; but this does not argue the formation of a compound which we are entitled to call sulphate of indigo. Such a solution differs in no respect from that of resins and other organic bodies in the same acid, or even from the solution of these substances in alcohol or ether.

" Those who are fond of speculating upon the manner in which the elements of water are arranged in organic bodies, may find it curious that sulphuric acid should abstract water from indigo, and not from cerulin, a substance which contains three times as much oxygen and hydrogen ; or that the same acid which robs indigo of its water, should immediately restore three times as much.

*On a new Substance produced from Indigo by means of Sulphuric Acid.*

" While engaged with these experiments, I discovered, that if the action of sulphuric acid upon indigo be stopped at a certain point, a new substance, altogether different from cerulin, is produced, possessing rather singular properties. It is formed at the instant that indigo changes from yellow to blue by the action of sulphuric acid.

" By the following process, it is obtained of greater purity than by any other method I have been able to discover. Prepare a quantity of indigo by boiling it in sulphuric acid diluted with three parts of water, and drying, after it is well washed. By such treatment, it is deprived of more than a third of its weight of impurities. Mix one part of this purified indigo with seven or eight parts of concentrated sulphuric acid in a stoppered phial, and agitate the mixture occasionally, till it becomes of a bottle-green colour. Then mix it with a large quantity of distilled water, and throw it

upon a filter. By continuing to wash the filter with distilled water, the liquid which at first passes through colourless becomes more and more blue, and after some time all the indigo which has been changed passes through. The colourless washings must be thrown away. The blue liquid contains the new substance in solution, and does not differ in appearance from a solution of cerulin. On the addition of muriate of potash, the new substance precipitates of a most beautiful reddish-purple colour, exactly similar to the colour of the vapour of indigo. Let this precipitate be thrown upon a filter, and washed with distilled water, till the liquid which passes through forms no longer a whitish, but a red precipitate with nitrate of silver. It may then be dried.

" From the property possessed by this substance of becoming purple-coloured on the addition of a salt, I have called it *phenicin*, from the Greek word *φοινίξ*, purple; and, to prevent circumlocution, I shall hereafter make use of this term.

" This substance, prepared with muriate of potash, is, when dry, of a brownish black colour. Heated in a crucible, it gives off a little vapour of indigo. I was at first uncertain whether this might not proceed from indigo formed by the decomposition of part of the phenicin by the heat; but I shall state a fact which shows that the indigo may have another source, and that it may exist in a small quantity in the purple substance. After the filter is washed till the washings are very slightly blue-coloured, the liquid that passes through is precipitated blue, instead of red, by muriate of potash, and the precipitate consists of indigo with a little phenicin. Thus it appears that even indigo is, in certain circumstances, capable of dissolving in water. By drying the phenicin, prepared as I have stated, and redissolving it, a small quantity of indigo remains; but still the phenicin yields a little purple vapour when heated.

" When the purple substance is burnt, it leaves about fifteen per cent. of ashes, which dissolve in water, and consist of sulphate and muriate of potash.

" Phenicin dissolves both in water and alcohol, and the solution in both cases is blue. It is precipitated again of its original purple colour by all saline substances whatever. Different salts, however, possess different powers of precipitation. Thus muriate of ammonia, chlorate and prussiate of potash, and muriate of soda, precipitate the phenicin entirely from about sixty times their weight of any aqueous solution; and nitrate, muriate, and sulphate of potash, from about 100 times their weight. But the sulphates of magnesia, zinc, and copper, precipitate 2000 times their weight of a solution of phenicin; sulphate of iron about 3000 times, and alum and muriate of lime as much as 8000 times.

" The phenicin being previously combined with a salt of potash, is not



altered by being again precipitated by any alkaline salt. These salts do nothing more than saturate the water to such a degree that the substance is no longer capable of dissolving in it. But the earthy and metallic salts combine with this substance, and displace the salt of potash previously united with it; and I have observed very little difference in the quantities necessary to precipitate solutions of different strengths. The precipitates formed by lime, barytes, alum, and copper, are totally insoluble in pure water, however well they may be washed. Those formed by iron and magnesia dissolve to a small extent, when freed from their former menstrua by filtration. Their solution is purple-coloured.

"Acids have no effect in preventing the precipitation of phenicin by saline bodies; and the precipitates once formed are not redissolved in the same liquid by the assistance of heat.

"The method which I have given for preparing the new substance is tedious. As only a small part of the indigo is converted into phenicin, the quantity obtained each time is very small, and requires a great quantity of distilled water, and a long time to filter. But if we allow the indigo to be wholly converted into phenicin, its solution cannot be made to pass through any filter, however porous, or however well washed it may have been with water or ammonia. It was by accident that I discovered the possibility of filtering it when only a small portion of the indigo had had time to be changed; and it was only by preparing it in this manner that I found the purple colour to be owing to the presence of saline matter, and its own colour to be like that of cerulin.

"The following is a method of preparing this substance in greater quantities, though not so pure. Mix together one part of indigo in powder, and ten parts of concentrated sulphuric acid, in a phial, and agitate from time to time, till the blue colour, which the indigo loses at first, is completely restored. This, at the ordinary heat of summer, requires nearly three hours. At 100° Fahr. it is effected in about twenty minutes; and indigo mixed with sulphuric acid, at the heat of boiling water, becomes blue the instant the mixture is made. At 45° Fahr. ten or twelve hours are necessary; and at lower degrees of heat, a still longer time, supposing always the quantity of materials small enough to cool very soon after mixture to the stated point. Pour this mixture into a large quantity of distilled water, and filter. Take the precipitate off the filter, wash it well with distilled water containing the proportion of muriate of ammonia necessary to prevent the substance from dissolving in it, and filter again. Dissolve anew the precipitate in a large quantity of distilled water; heat the solution to drive off any particles of air which might prevent the impurities from subsiding, and let it stand two or three days in a tall vessel. Then draw off with a syphon as much as may be thought perfectly clear, leaving

the remainder to be washed with more distilled water. Add to the solution any alkaline salt, till the substance be precipitated; then throw it upon a filter, and wash with distilled water till the liquid refuses to pass through.

"When a solution of phenicin is precipitated, the liquid that remains is always more or less coloured with cerulin; and however often this be repeated upon the same material, a little cerulin is always left. If it has been heated, more cerulin is formed. It follows from this that phenicin is changed into cerulin by the action of water alone.

"Phenicin dissolves in the water of liquid ammonia without injury; but the fixed alkalies destroy it, though not very readily. Chloride of tin precipitates the solution, but gradually redissolves the precipitate, forming a yellow solution; and the phenicin is thrown down again of its own colour, by the salts of copper.

"Phenicin dissolves readily in concentrated sulphuric acid, forming a blue solution; and if this be poured immediately into water, the greater part of it is precipitated again, the impurities of the acid being sufficient to prevent its solution in water. A portion is converted into cerulin, which remains in solution. When allowed to remain dissolved in sulphuric acid, it is soon entirely converted into cerulin; consequently, in preparing phenicin by the second process, it is impossible to prevent the formation of a certain portion of cerulin.

#### *Constitution of Phenicin.*

"The facts which I have stated, to prove that cerulin differs from indigo only containing more or less water, equally apply to this substance.

"One grain of pure phenicin produced 5.085 cubic inches of dry carbonic acid gas, which contain 0.6462 grains of carbon. Hence, calculating as in the case of cerulin, the substance consists of

Carbon . . . . .	64.62
Azote . . . . .	9.91
Oxygen . . . . .	21.49
Hydrogen . . . . .	3.98
	<hr/>
	100.00

This is very nearly indigo + 2 water, and its atomic proportions may be thus stated:—

1 atom azote . . . . .	1.75	or 9.46
4 atoms oxygen . . . . .	4.00	21.62
6 atoms hydrogen . . . . .	0.75	4.05
16 atoms carbon . . . . .	12.00	64.87
	<hr/>	<hr/>
	18.50	100.00

"The experiments of Mr. Smithson, related in the Philosophical Transactions, have given us very correct ideas on the nature and number of the vegetable colouring matters. It is sufficiently obvious that phenicin is not the principle which colours any of the purple or blue vegetables examined by that chemist. I collected a number more of such purple flowers as are most commonly met with, and dipped them separately in concentrated sulphuric acid; but instead of becoming blue, they were uniformly changed to red, and formed red-coloured solutions on the addition of water. Future inquiries, therefore, must determine whether phenicin exists ready formed in nature, either in the blue or in the purple state.

"Alcohol modifies remarkably the action of sulphuric acid upon indigo. A mixture of three parts of alcohol of specific gravity 0.84, and two parts of acid, dissolves indigo without rendering it yellow, and the solution may even be filtered through strong paper. Probably a larger quantity of pure alcohol might be employed. On the addition of water, the indigo is precipitated without alteration; and if common indigo has been used, resin precipitates along with it. It may remain dissolved in this mixture any length of time without conversion into phenicin. A solution of phenicin in sulphuric acid may also be mixed with alcohol without precipitation, and the acid is rendered incapable of converting it into cerulin."

Mr. Holt states that the solution of indigo in sulphuric acid is completely deprived of colour by adding to it filings of zinc or iron. Whenever the colourless, or slightly grey-coloured solution, suffers the contact of air, the blue colour reappears. It was previously well known that sulphuretted hydrogen blanched the above solution of indigo.

#### NOTE HH. p. 290.

A VALUABLE paper on the cultivation of woad in England was published by Mr. John Parrish in the 12th volume of the Letters of the Bath Agricultural Society. It is reprinted in Tilloch's Magazine, vol. xxxviii. p. 43.

#### NOTE II. p. 341.

THE first person who established in this country a factory for dyeing Adrianople madder-red, was M. Papillon, who in the year 1790 obtained a premium from the Commissioners and Trustees for Manufactures in Scotland, for communicating the details of it to Dr. Black, on condition that it should not be divulged for a certain term of years, during which M. Papillon was to have the sole use of his own secret. The term being expired, the process was published. It resembles pretty closely the method described in the text by M. Berthollet. Those who wish to compare them, will find M. Papillon's in the 18th volume of Tilloch's Magazine, p. 43.

M. Vitalis, in his valuable treatise on dyeing, published in 1823, (*Cours Élémentaire de Teinture*), has entered at considerable length into the description of the Turkey-red dye, with which his situation at Rouen had made him familiar. I shall here note those points in which he appears to differ from M. Berthollet, or is more precise.

In the *second* operation, he states, that from 25 to 30 pounds of sheep's dung are commonly used for 100 pounds of cotton yarn. The dung is first steeped for some days in a ley of soda, of 12° or 14° Tw. This is afterwards diluted with about 125 gallons of a weaker ley, and at the same time bruised with the hand in a copper basin, whose bottom is pierced with small holes. The liquor is then poured into a vat containing five or six pounds of fat oil, (*Gallipoli*), and the whole are well mixed. The cotton is washed in this, as prescribed by M. Berthollet. The hanks of cotton yarn are then stretched on perches in the open air, and turned from time to time, so as to make it dry equally. After receiving thus a certain degree of desiccation, it is carried into the drying house, which is heated to 50° Reaumur, (144° Fahrenheit,) where it loses the remainder of its moisture, which would have prevented it from combining with the other mordants, which it is afterwards to receive. What is left of the bath is called *avances*, and is added to the following bath. Two, or even three dung baths are given to the cotton, when it is wished to have very rich colours. When the cotton has received the dung baths, care must be taken not to leave it lying in heaps for any length of time, lest it should take fire; an accident which has occasionally happened.

#### *Third Operation.—Oil or White Bath.*

This bath is prepared by pouring in six pounds of fat oil, 12½ gallons of soda ley, at 1° or sometimes less, according as, by a preliminary trial, the oil requires. This bath ought to be repeated two, three, or even a greater number of times, as more or less body is to be given to the colour.

#### *Fourth Operation.—Salts.*

To what remains of the white bath, and which is also styled *avances*, about 25 gallons of soda ley, of two or three degrees, are added. Through this the cotton is passed as usual. Formerly, it was the practice to give two, three, or even four salts. Now two are found to be sufficient.

#### *Fifth Operation.—Degraissage.*

The cotton is steeped for five or six hours in a tepid solution of soda, of 1° at most; it is set to drain, is then sprinkled with water, and at the end of an hour is washed, hank by hank, to purge it entirely from the oil.

What remains of the water of *degraisage*, serves for the scouring, or *first* operation.

*Sixth Operation.—Galling.*

For 100 pounds of cotton, from 20 to 25 pounds of galls in sorts must be taken, which are bruised and boiled in about 25 gallons of water, till they crumble easily between the fingers. The galling may be done at two operations, dividing the above quantity of galls between them, which is thought to give a richer and more uniform colour.

*Seventh Operation.—Aluming.*

The aluming of 100 pounds of cotton requires from 25 to 30 pounds of pure alum, that is, alum entirely free from ferruginous salts. The alum should be dissolved without boiling, in about 25 gallons of river or rain water. When the alum is dissolved, there is to be poured in a solution of soda, made with the sixteenth part of the weight of the alum. A second portion of the alkaline solution must not be poured in till the effervescence caused by the first portion has entirely ceased,—and so in succession. The bath of saturated alum, being merely tepid, the cotton is passed through it, as in the gall bath, so as to impregnate it well, and it is dried with the precautions recommended above. The dyers who gall at two times, alum also twice, for like reasons.

*Eighth Operation.—Washing away the Alum.*

*Ninth Operation.—Maddering.*

For twenty-five pounds of cotton,  $6\frac{1}{4}$  gallons of blood are prescribed and 100 gallons of water. Whenever the bath begins to warm, fifty pounds of madder are diffused through the bath. Sometimes the maddering is given at two operations, dividing the madder into two portions.

*Tenth Operation.—Brightening.*

The brightening bath is prepared always for 100 pounds of cotton, with from four to five pounds of rich oil, six pounds of Marseilles white soap, and 150 gallons of soda ley at  $2^{\circ}$ .

*Eleventh Operation.—Rosin.*

This is done with solution of tin, mixed with soap water.

Two systems for Turkey red are known at Rouen. The first is called the grey course, the second the yellow; (*marche en gris*, and *marche en jaune*.)

The grey course takes its name from the cotton being subjected to the

maddering immediately after it has received the oily preparations, and the mordants of galls and alum, which give it a grey colour.

The yellow course is so called, because in this system the cotton, after having received a first time the oily preparations, as well as the mordants of galls and alum, is not exposed to the maddering till it has passed a second time through the same preparations and the same mordants, which give it a yellow colour. It is this second manner of working the Turkey red, which is called, in the phraseology of the dye-house, remounting on the galls.

The following table exhibits the difference which exists between these two courses :—

<i>Grey Course.</i>	<i>Yellow Course.</i>
Boiling	Boiling
Dung baths	Dung baths
White baths	White baths
Salts	Salts
<i>Degraissage</i>	<i>Degraissage</i>
Galling	Galling
Aluming	Aluming
Washing off the alum	Washing off the alum
Maddering	White baths
Brightening	Salt
Rosing	<i>Degraissage</i>
	Galling
	Aluming
	Washing off the alum
	Maddering
	Brightening
	Rosing

The grey course, as well as the yellow, is susceptible of a great many combinations and varieties, both in the order and number of the operations relative to each. The following are some examples with developments, which cannot fail to interest dyers.

*Grey Course for 100 Pounds of Cotton.*

*Scouring* in a soda liquor at  $2\frac{1}{4}^{\circ}$ , or with the waters of *degraissage* at  $2^{\circ}$ .

*Dung bath*, with 25 pounds of dung, and six pounds of oil—store-drying.

*Dung bath*,—idem—drying—idem.

*White bath*, with five pounds of oil, and soda liquor, at  $1^{\circ}$ ,  $1\frac{1}{4}^{\circ}$ , or  $2^{\circ}$ —drying.

*White bath*,—idem—drying.

*One or two salts*, the first at 2°, the second at 3°—drying.

*Degraissage* in pure water of a temperature equal to that of the atmosphere in summer, and between 15° and 18° Reaumur (66 and 72° Fahr.) in winter. The cotton is kept in the water for an hour or two. It is then taken out, wrung at the jack, and dried.

*White bath*, as above.

*White bath*, idem.

*White bath*, idem.

*Degraissage*, as above, with this difference, that it is washed well before wringing, and then dried.

*First galling*, with seven pounds of galls in sorts, or galls of Istria—drying.

*Second galling*, with 14 pounds of sumach, which is just brought to boil; it is then refreshed (with cold water), passed through a sieve, and the cotton is turned through as hot as possible—drying.

*First aluming*, with 18 pounds of purified alum; it gets next a slight washing, but is not dried.

*Second aluming*, with 12 pounds of the same alum—thorough washing—wringing—no drying.

*Maddering*, with seven quarters of a pound of Provence lizari for every pound of cotton. Only 25 pounds are dyed at a time, which must be allowed to cool after coming out of the boiler before it is washed; then it is to be wrung, but not dried.

*Brightening*, with soda liquor at 1½°, or with what remains of the water of *degraisage*; to which three or four pounds of white soap may be added. The cotton must be boiled for four or five hours in a copper closed with a cover, but not so tight as to hinder the steam from escaping. The ebullition is to be kept up, till a pattern, which has been observed from time to time, has reached the proper point. The cotton is allowed to cool in the boiler, is then well squeezed, washed in the river, wrung at the jack and pin, and, without drying, subjected to the next operation.

*Rosing*, with 12 pounds of white soap dissolved in a sufficient quantity of water. When the soap is dissolved, there is poured into the copper a solution of a pound or a pound and a half of salt of tin in two quarts of lukewarm water, to which about a third of a bottle (*bouteille*) of nitric acid at 36° of the areometer has been added. It is made to boil for four or five hours, and the cotton is withdrawn whenever a pattern has attained the proper hue.

If the first rosing do not bring the cotton to the desired tint, a second, similar to the preceding, may be given; but only eight pounds of soap should be employed.

*Yellow Course, in like manner, for 100 Pounds of Cotton.*

*Scouring*, as in the grey course.

*Two baths of sheep's dung*, each along with five or six pounds of oil—drying.

*Two white baths*, each with six or eight pounds of oil—drying.

*Two salts*, each at 2° of the hydrometer of Baume, (2½° Tw.)

*Degraissage*, as usual—washing—then drying.

*First galling*, with eight pounds of nut-galls—drying.

*First aluming*, with thirteen pounds of pure alum—washing without drying—wringing, and drying.

*Three white baths*, each with six pounds of oil—drying.

*Two salts*, each at 2°—drying.

*Second galling*, with four pounds of galls, and twelve pounds of sumach—drying.

*Second aluming*, with thirteen pounds of pure alum—drying.

*Washing off the alum* very carefully—wringing—drying or not, at pleasure.

*Maddering*, with two pounds of lizari of Provence per pound of cotton.

*Brightening*, as in the grey course.

*First rosing*, as in the grey course.

*Second rosing* (if wanted) as in the grey course.

The system of operations indicated in either of the above courses, appears to M. Vitalis so preferable to every other, that he wishes dyers to follow them, leaving them always at liberty to give baths a little more charged with oil, more of them, or some additional salts, &c.

The grey course is usually followed for making the ordinary Adrianople reds; and the yellow course is reserved for reds of the first quality in point of lustre and durability.

It is also by the yellow course that linen or hemp must be treated.

M. Vitalis states, in his *Manuel du Teinturier*, that the bisulphate of potash may be used instead of the salt of tin for rosing, and that it gives to the red a peculiar shade very agreeable to the eye. In vain, he observes, should we attempt to give a fine red with only 25 pounds of oil for 100 of cotton. No less than 40 pounds are employed, and very commonly 50, or even more. Nor will sumach replace the galls; nor will a lower heat answer in the drying-stove.

The *avances* (residuary liquors) in which the cotton has been worked after the galling are good for nothing, and must be thrown away. When the Adrianople red is finished, the colour is much improved by preserving the cotton for one or two months shut up pretty tight in hempen bags.



This seems to show that the mordants have not completely exhausted their action in the operation itself, and that the affinities between them and the colouring matter require a certain time to produce their whole effect.

A good Adrianople red supports for ten minutes\* the action of nitric acid at 28° Tw., without suffering any sensible change. By letting it remain longer in the acid, or by employing a stronger one, the cotton becomes more and more orange, and finally loses its colour. The simple madder reds, exposed to the same test, disappear in less than three minutes.

Cottons which have not been suitably worked in the preparations, come out of the maddering with a thin colour, sometimes of a brick hue. Before brightening these cottons, they ought to get new oil baths, and the operations should be repeated as if they had not been dyed. The brightening and rosing will have a little less power than in ordinary cases. Cotton dyed Turkey red is sometimes too much charged with oil, and the excess rises in time to the surface of the cotton, or of the stuffs made from them. The surface is then sprinkled with small white points, which alter the beauty of the colour. This inconvenience is remedied by dipping the cotton for some time in, or by passing it or the stuffs through, a hot bath of soap. Ten or twelve pounds are sufficient for 100 pounds of materials.

Cotton yarns for warp being more twisted than those for woof, require more manipulation to give them an equally good colour.

The object of the scouring, or first operation in the Turkey red process, is to free the stuff to be dyed from an oily or resinous matter which envelopes their fibres, and fills the interstices between their filaments. It is this oily or resinous matter which renders these substances less white, and which weakens their affinity for water, and for the colouring matters which they are to receive. The baths of sheep's dung have been supposed to make the cotton or linen fibres approach more to the nature of animal substances. This albumino-gelatinous matter, dissolved in the alkaline ley of soda, is in the most favourable state for entering into combination with the cotton.

The white baths, which follow those of dung, co-operate with the latter, giving to the cotton the oily principle, for which cotton is known to have a great affinity, and which, moreover, enjoys the property of combining with the colouring matter.

But the superfluous quantity of oil, diffused merely on the surface of the fibres, would obstruct the assumption of the dye, and is therefore to be removed by the *degraisage*; an operation much more important than is commonly imagined, and which therefore requires to be conducted with every possible care.

The washings have in general the same object as the *degraisage*, and require the same attention.

As to the desiccation, which must be performed after the greater part of the operations, its necessity will readily be recognized, by considering that the moisture introduced into the cotton by the application of a first mordant, would necessarily become an obstacle to the introduction and combination of a subsequent mordant. For this reason, it is not sufficient always to dry in the air, but the desiccation must be completed in a stove heated to 50° or 55° Reaumur, (144° to 156° Fahr.,) especially during winter, and when the weather is moist.

It will be impossible to give a good explanation of the process of galling till the principles furnished by the nut-galls be more exactly known. It appears certain that they contain a peculiar acid, named from them the *gallic*. But what is the nature of the tannin which always accompanies that acid? The galls probably form not only an energetic mordant, by operating directly on the cotton which has received the oily preparations, but also act by attracting the alumina.

The alum plays a very important part in Turkey red dyeing, but its functions are not altogether explained. Some drops of the decoction of galls poured into a solution of alum determine, according to the late Mr. Henry, a precipitate of a white colour, which appears to be alumina separated from the sulphuric acid. When galled cotton is passed through a solution of alum, it may therefore be supposed that a portion of the alumina is attracted to the cloth by the agency of the galls. The temperature of aluming ought to be rather low, viz. 18° or 20° Reaumur, (about 75° Fahr.,) since, at a greater heat, the alumina might be too rapidly and abundantly thrown down, and much of what is so hastily deposited might not combine with the galls. This compound of galls and alumina forms a complex mordant, which unites with the mordants that the oily principle and the dung have already furnished.

We may also remark, that it is not without reason that, in the aluming for Turkey red, the precaution is taken of adding to the ordinary alum a certain quantity of alkali (an ounce of soda to a pound of alum.) Perhaps the oily baths contribute to the fixation of the alumina, forming with this earth a species of aluminous soap, so much the more permanent, as it is altogether insoluble in water. But the alkali must not be caustic, as Macquer had conjectured; for alumina, dissolved from alum in a caustic ley, will not answer for furnishing a mordant to the Adrianople madder-red. The blood adds no colouring matter to the madder in the dyeing operation. The dull and dark red which the cotton takes in the madding is by no means an agreeable shade. This sombre hue must be removed from it, and a bright decided red brought out. This effect is

obtained by the brightening, which lays bare the red tint that had been masked by the brown colouring matter, which is dissolved and carried off by the brightening bath.

By the *rosing* the cotton acquires a lustre and vivacity far superior to what the *brightening* can give. To obtain this effect, the cotton is set to boil for four or five hours, as has been stated, in a solution of white soap, to which a solution of salt of tin (muriate) is added, along with a certain quantity of nitric acid, at 66° Twaddell. It would seem that in this operation the soap and the salt of tin mutually decompose one another,—that the muriatic, as well as the nitric, which are added, seize the soda constituent of the soap,—that the oil separated from the alkali unites to the oxyde of tin to form an acid metallic soap, whereby the red is finally brightened, acquiring that lustre so pleasing to the eye.

The following process is that followed by a practical dyer of Turkey red in Scotland, for 1 cwt. of cloth or yarn :—

First, Boil the goods with white soap and pearl ash, or soda ley. Twelve pounds of white soap are dissolved in water, in a copper, along with six gallons of the ley, pretty strong. The boiling is continued for five or six hours.

Second, The sheep's dung liquor. To make this, take twelve gallons of soda liquor, 3° Tw. (sp. gr. 1.015,) two gallons Gallipoli oil, six gallons of sheep's dung, twenty-four gallons of soda liquor, 5° Tw. (sp. gr. 1.025.)

Tramp the cloth or yarn well in this liquor, then hang it in the air to dry, and next in the stove.

The dunging is repeated a second and a third time, as above, drying the goods after each repetition.

The yarn or cloth is to be steeped all night in warm water, at 100° Fahr. with four gallons of soda liquor, 12° Tw. (sp. gr. 1.060.) Out of this it is to be well wrung next morning, hung in the air, and, lastly, dried in the stove.

Take now twelve gallons of weak soda liquor, 3° Tw. (sp. gr. 1.015,) Gallipoli oil, two gallons, soda liquor, 5° Tw. (sp. gr. 1.025,) thirty gallons. Tramp the cloth or yarn in this mixture three or four times; then put in the air, and finish in the stove every time.

#### *Steep for cleaning away the Oil.*

Steep the goods in warm water at 140° Fahr., with four gallons of soda liquor for each cwt. Wring it out next morning, wash well and dry it, when it is ready for the galls.

#### *Gall Liquor.*

Take twenty-four or twenty-five pounds of nut-galls, and boil them for eight hours. Take the clear liquor, and tramp the cloth or yarn as warm

through this liquor as the skin can bear ; wring, put in the air, and then in the stove.

*Alum Liquor.*

Take 25 pounds of alum,—dissolve in warm water ; add 4 gallons of soda, 12° Tw. (sp. gr. 1.060.) Next morning take the clear liquor, put it into a copper, and warm it as hot as the hands can bear. Tramp the stuff through this liquor, wring, and put in the stove to dry.

*Second aluming as above.*

Steep the alumed goods in lukewarm water all night, next day wash them well in the river, then they are ready for drying.

*To dye twelve dozen of Cloths, (Pieces.)*

Allow 2 pounds of madder to each pound of cloth, bring to the boiling point in an hour, and keep boiling for half an hour. Then enter the goods into the copper, adding 2 gallons of blood well mixed. (The blood should surely be added to the cool, or merely tepid water.) Let the goods be now well washed and dried. For the *cue*, take half soda and half pearl ashes, half a gallon of oil, add as much water as will bring the liquor to No. 6 of the hydrometer, (sp. gr. 1.030.) But the oil must have been previously mixed with twelve gallons of soda liquor, 3° Tw. (sp. gr. 1.015.) Put the goods through this liquor as through the white bath ; wring and stove-dry.

*For Clearing.*

Fill a copper with clean water ; dissolve 4 or 5 pounds of white soap in it, and half a pound of pearl ashes. Boil slowly from six to eight hours ; then wash and wring the goods. Lastly, fill a copper with clean water, adding a pound or two of white soap, and boil the goods an hour or two.

They are now finished.

Mr. John Thomson of Glasgow published in the *Annals of Philosophy*, vol. viii. p. 463, some ingenious ideas on the theory of the Turkey red process. "Silk and worsted," says he, "have a natural varnish which cotton does not possess." To supply this defect, the repeated immersions, followed by exposure to the atmosphere, and to the heated air of a stove, may give the oil the proper consistency, by the absorption of oxygen, for forming a varnish, with which the colouring matter unites, and through which it may be said to shine, which causes that superior brilliancy which the goods attain when they are cleared, or, as it may be called, polished. I therefore presume, that the fixedness and brilliancy of the colour will depend on the quantity of oil imbibed, as every repetition of drying pre-

sents new fibres to be varnished with an additional quantity ; for I have always found, that the permanency was in proportion to the number of manipulations in the saponaceous liquor, and a proportionable freedom could also be used in reducing or clearing. The white immersions, omitting the sheep's dung, are just applying successive coats of varnish. Clearing is never attempted from the madder copper, without immersing the goods again in soda and oil, and drying them in a stove, which I consider to be also supplying them with an additional coat.\*

The alkaline ley occasions a greater separation in the particles of the oil, by which it combines more closely with the fabric of the cloth. The sheep's dung in the first immersions may serve as a covering or great coat, to keep the goods moist for a considerable time, that they may more fully imbibe the liquor, by preventing the evaporation from being too quick in the great heat to which they are exposed.

After the frequent immersions the cloth feels like leather, no doubt from a superfluity of liquor. It is then steeped in a ley of carbonate of soda, and afterwards well washed and dried, as a preparation for the galling and aluming. The astringent principle has been long known for darkening and fixing common red colours on cotton, by uniting with the earth of alum, and strengthening the basis. To the use of blood in the madder copper I attribute nothing ; as in the rancid and putrid state in which I have seen it used, were it not for the prejudice of the operator, it might be safely dispensed with.

In proof of the above idea, that it is only the oil uniting with the earth of alum that is of use, I may refer to the mode of dyeing that colour in the East, quoted by Dr. Bancroft, viz. soaking their cotton in oil, (no matter of what description,†) during the night, and exposing it to the sun and air during the day, for seven successive days, rinsing it only in running water, and then immersing it in a decoction of galls and the leaves of sumach previous to aluming.

I would therefore request the practical dyer, who wishes to arrive at a knowledge of this unaccountable process, to give up the idea of animalization, if by it be meant impregnating the cloth with an animal matter, and by the power of the microscope, or any better method, look for the whole truth from some other source than chemical analysis. I am at present inclined to believe that it is a mechanical operation united to a chemical, and that the frequent immersions in the imperfect soap are equivalent to laying on the first, second, third, &c. coats, preparatory to finishing a fine painting in oil.

\* In the French processes given above, the brightening follows the maddering without any immediate oil steep.—*Translator.*

† Olive oil, hog's lard melted, oil of sessamum, &c. have all been used with success.

A very eminent calico manufacturer, whom I consulted on the Turkey red process, assured me, that the only essential mordants are oil and alumina : and that bright and fast reds, equal to any produced by the usual complicated process with sheep's dung, galls, and blood, may be obtained without these articles.

*Dyeing Cotton of a Smoke-red (rouge enfumé.)*

Smoke-red is a name given to a dull red without lustre, which resembles the burned red (*rouge brûlé*) of the India handkerchiefs. To dye this colour, the following method will answer.

1. Preparations of the Adrianople red, according to the grey course above prescribed, down to the maddering, inclusive.

2. The cotton, when washed and dried, receives a strong mordant of acetate of alumina ; that is to say, at 6° of the areometer of Baumé (8° Tw.) and at a temperature of about 70° Fahr. After this it is dried, and then it receives a good washing.

3. It is passed through a bath of quercitron of greater or less strength.

4. After being dried and washed, it is brightened in a soda liquor with soap.

*Dyeing Cotton of a Cherry and Rose-red.*

The cherry-red is pretty certainly obtained by following the process which we shall point out.

Boiling.

Bath of sheep's dung.

Three white baths, each with 6 or 8 pounds of oil.

A salt at 2° Baumé, (2½° Tw.)

A careful *degraissage*.

Galling with a decoction of 5lbs. of nut-galls, to which the infusion of 20lbs. of sumach is added.

Aluming with 36lbs. of very pure alum.

Careful washing away of the alum.

Maddering with the madder of Cyprus or Smyrna, in the proportion of a pound or pound and a half for every pound of cotton. There may, however, be mixed in a third of Provence madder, with two-thirds of the above madders. Brightening, by boiling the cotton for five or six hours in a ley of soda, at 1½° Baumé (2° Tw.), in which from 8 to 10 pounds of soap have been dissolved. The cotton is allowed to cool in the bath, and then washed. (The brightening may be also very simply effected, by passing the cotton through a weak solution of chloride of potash or lime.)

Rosing. The cotton is boiled during half an hour in 150 gallons of water, in which has been dissolved a pound and a half of salt of tin, pour-

ing in afterwards a bottle (quart) of sulphuric acid, at 30° Baumé. (52° Tw.) On coming out of the boiler it is washed with care, then boiled anew, for three quarters of an hour, in a solution containing from 15 to 16 pounds of white soap.

For procuring the rose colour, the strength of the brightening is a little increased, and there is employed in rosing somewhat more sulphuric acid at first, than there is white soap in the succeeding bath.

The brightening in the liquor of Javelle (blacking liquor) suits well here. The rose may also be given, by using oily preparations not so highly charged, less mordant, and consequently less madder, in the dyeing bath.

A little experience will remove all obstacles.—*Vitalis*.

#### NOTE KK. p. 347.

WE are indebted to MM. Pelletier and Caventou for a chemical investigation of cochineal, in which its colouring matter was skilfully eliminated. Their principal researches were directed to the mestèque cochineal (*coccus cacti*), though a few experiments were also made on some other kinds.

Purified sulphuric ether acquired by digestion with it a golden yellow colour. This infusion left, on evaporation, a fatty matter of the same colour.

Cochineal, exhausted by ether, was treated with alcohol at 40°. After thirty digestions in the apparatus of M. Chevreul, the cochineal continued to retain colour, although the alcohol had ceased to have any effect on it. The first alcoholic liquors were of a red verging on yellow. On cooling, they let fall a granular matter. By spontaneous evaporation, this matter, of a fine red colour, separated, assuming more of the crystalline appearance. These species of crystals dissolved entirely in water, which they tinged of a yellowish-red. Treated with very strong alcohol in the cold, they re-dissolved, leaving a very animalized brownish matter, to which we shall afterwards return, since we shall find this matter in greater abundance in the watery decoctions of cochineal previously exhausted by ether and alcohol.

The alcoholic solution of these crystals, thus deprived of its animalized matter, is still susceptible of affording the above crystalline sediment. In this state, although free from animalized matter, especially when they have been re-dissolved and recovered anew, these crystals do not, however, present the colouring matter pure, as was at first believed. If this matter be treated with sulphuric ether, one portion is dissolved and colours the ether orange-yellow; and it is only after the ether has ceased to have any action on the mass, and when it comes off colourless, that the substance which will not dissolve in the ether may be regarded as the colouring principle, if not absolutely pure, at least very nearly so. The colouring principle

of cochineal, insoluble by itself in ether, may, however, be dissolved in small quantity in this liquid, through the intervention of the fat crystallizable matter, while the latter becomes less soluble in ether, as it is enveloped and protected by a quantity proportionally greater of the colouring principle. These considerations led MM. Pelletier and Caventou to make the following experiment, in the hope of stripping the colouring matter of every particle of the fat substance. They dissolved a certain quantity of their coloured crystals in very strong alcohol, and added a quantity of sulphuric ether equal to that of the alcohol employed. The mixture became turbid, but at the end of some days it had grown perfectly clear. It was of a red colour inclining considerably to yellow. A good deal of the colouring matter had, however, fallen down on the bottom of the vessel, forming an incrustation of a magnificent purple-red. This matter, treated with ether, no longer yielded any principle; and the properties to be presently detailed lead to the belief, that it may be regarded as the colouring matter of cochineal in a state of purity. By adding new portions of ether to the decanted liquor, a certain quantity of colouring matter may again be thrown down. The alcoholic tinctures in which the first crystals were formed, were evaporated to dryness on the water-bath; and the colouring matter obtained, treated by methods analogous to the preceding, afforded likewise fat crystallizable matter and colouring principle.

*Of the Colouring Principle of Cochineal.*

This matter has a very brilliant purple-red colour; it adheres strongly to the sides of the vessels; it has a granular and somewhat crystalline aspect, very different, however, from those compound crystals alluded to above; it is not altered by the air, nor does it sensibly attract moisture. Exposed to the action of heat, it melts at about the fiftieth degree Centigrade (122° Fahr.) At a higher temperature it swells up, and is decomposed with the production of carburetted hydrogen, much oil, and a small quantity of water, very slightly acidulous. No trace of ammonia was found in these products.

The colouring principle of cochineal is very soluble in water. By evaporation, the liquid assumes the appearance of syrup, but never yields crystals. It requires of this matter a portion almost imponderable to give a perceptible tinge of bright purplish-red to a large body of water. Alcohol dissolves this colouring substance; but, as we have already stated, the more highly it is rectified, the less of it does it dissolve. Sulphuric ether does not dissolve the colouring principle of cochineal, but weak acids do, possibly owing to their water of dilution. No acid precipitates it in its pure state. This colouring principle, however, appears to be



precipitable by all the acids when it is accompanied by the animal matter of the cochineal.

Acids, however, change the colour of this substance, converting it into a bright red, then a yellowish-red, and lastly, a yellow. When the acids have not been too concentrated, its proper colour may be restored by saturation with alkali. Chlorine changes the colour of this principle to yellow, and then destroys it altogether. It produces no precipitate in its solution, unless it contains animal matter. Hence chlorine becomes a useful re-agent for trying the purity of this colouring substance. Iodine acts like chlorine, but more slowly. The alkalies, poured into a solution of the colouring principle of cochineal, change its hue to crimson violet. If the alkali be immediately saturated, the original colour is restored, and the colouring matter may be recovered without any remarkable alteration in its principal properties. If the action of the alkali has been longer continued, or aided by heat, the violet shade disappears, and the colour passes back to red, and then yellow. In this case, the colouring matter is totally altered, for by putting it into contact with those metallic salts which form with it insoluble combinations, we obtain precipitates entirely different from those which the pure colouring matter produces with the same salts.

Lime-water produces a violet precipitate with the colouring matter of cochineal. Barytes and strontites do not occasion any precipitate in a solution of the colouring matter; but they change the hue to violet like alkalies. The affinity of alumina for the colouring matter is very remarkable. When that earth, newly precipitated, is put into a watery solution of the colouring principle, this is immediately seized by the alumina. The water becomes colourless, and a fine red lake is obtained, if we operate at the temperature of the atmosphere; but if the liquor has been hot, the colour passes to crimson, and the shade becomes more and more violet, according to the elevation of the temperature, and the continuance of the ebullition.

If, before adding alumina to the watery solution of the colouring principle, some drops of an acid be poured into this, the lake obtained is at first of a brilliant red; but the slightest heat changes it to a violet hue. The same effect is produced by putting into the solution of the colouring principle some grains of an aluminous salt. But, on the contrary, if we add to the colouring principle a small quantity of alkali, potash, soda, ammonia, or their subcarbonates, and if we then diffuse through the solution some gelatinous alumina, the liquor rendered violet by the alkalies returns instantly to the red, by the formation of a lake which readily precipitates. In this case, we may keep the mixture boiling for a long time, without making the lake perceptibly violet. This property cannot, however, be

quite restored by alkaline saturation, especially if the action of the alkali has been some time continued. These facts may serve to explain several phenomena which have been observed in the operations of the scarlet or crimson dye.

Most salts exercise on the colouring matter of cochineal an action characterized by changes in the hue ; but only a small number are capable of precipitating it, when it is in a state of perfect purity.

Nitrate of silver has no action on it. The soluble neutral salts of lead change the red colouring matter to violet ; and the acetate of lead determines immediately an abundant precipitate. This precipitate keeps its tint, though there be an excess of acetic acid. By passing a stream of sulphuretted hydrogen gas through the combination, it is decomposed, and the colouring matter is then obtained in a state of purity. Protonitrate of mercury produces a violet precipitate in the solution of the colouring matter ; the deutonitrate precipitates less easily the colouring matter ; what falls is of a scarlet hue. Corrosive sublimate has no action on it. The salts of copper cause no precipitate, but change the colour to violet ; and the salts of iron give a brownish tint, without producing any precipitate. The salts of tin exercise on the colouring matter of cochineal a remarkable action. The protomuriate of tin forms a very abundant violet precipitate in the liquid. This precipitate verges on crimson, if the salt contains an excess of acid. The permuriate of tin produces no precipitate, but changes the colour to scarlet red. If gelatinous alumina be now added, we obtain a fine red precipitate, which does not pass to crimson by boiling.

The salts of lime, barytes, and strontian, perfectly neutral, equally change the colouring principle to violet ; but no precipitate can be obtained, except with sulphate of lime.

The aluminous salts, even slightly acidulous, make the colour pass to crimson, especially with the aid of heat ; none of them produce any precipitation : they even counteract the precipitation of the colouring matter by alumina, of which, in that case, a great excess is required to deprive of colour a liquor tinged with cochineal. Crimson, or even violet lakes, are then obtained.

The neutral salts of potash, soda, and ammonia, occasion a violet tinge, but no precipitate. The salts, with excess of acid, as the binoxalate and bitartrate of potash, change the colour to scarlet, but still without precipitation.

It appears, therefore, to MM. Pelletier and Caventou, that the metals susceptible of several degrees of oxydizement act like the acids when they are oxydized to a maximum, and like alkalies when they are in the lower stage of oxydizement ; and that this alkaline influence of certain oxydes

may be exerted in the midst of an acid liquid, when these oxydes are capable of forming with the colouring principle an insoluble compound, while it is totally destroyed by the excess of acid, if the oxyde can produce only soluble combinations, as is the case with soda and potash.

Tannin and astringent vegetable matters form no precipitates with the colouring principle of cochineal. This pure colouring principle was ignited with deutoxyde of copper, and yielded a gas composed of ninety-eight parts of carbonic acid and two of hydrogen. No appreciable portion of azote was obtained.

To this colouring principle the name *Carminium* has been given, because it forms the basis of the pigment called carmine.

The cochineal, after having undergone the action of ether and alcohol, was treated in the digester with water, till it ceased to give out colour. There then remained a translucent, gelatinous, brownish matter, of which some portions were white, insoluble in cold water, giving up to boiling water merely a portion of their substance, without any trace of colouring principle. The first watery decoctions were much coloured; the last were colourless. The water acts on cochineal, so as to carry off the last portions of the colouring matter, and the fat substance, and to dissolve a portion of the animal matter, which constitute, as it were, the basis or skeleton of this insect.

This white or brownish translucent animal matter, when exposed to a moderate heat, dries, takes a horny appearance, and can then be kept for a long time; but when, on the contrary, it is left in the moist state, it is spontaneously decomposed with the diffusion of a nauseous smell. At a higher heat, it furnishes all the products of animal matters, and particularly carbonate of ammonia. Boiling water slowly dissolves a little of the animal matter; and it putrefies with great readiness. It differs from gelatin, in not being thrown down from water by alcohol, and in being precipitable in whiteish flocks by all the acids.

Chlorine precipitates the animal matter of cochineal, but iodine produces no sensible effect on its solution. Potash and soda communicate to water the power of dissolving this animal matter in abundance. When they are neutralized by acid, the matter is recovered; but if the acid is in excess, it forms an insoluble compound with an animal matter. All the salts with excess of acid precipitate the animal matter, and are brought to the neutral state. Thus the precipitate seems formed of the animal matter and of the acid that is in excess. But several of the neutral salts are decomposed by the animal matter, and precipitates are obtained containing it, the metallic oxyde and the acid. In this way, the salts of lead, copper, and tin, act. The nitrate of silver also possesses this property; and since this salt does not precipitate the colouring matter of cochineal,

while it is very sensible in regard to the animal matter, it forms a good re-agent of the purity of carminium.

The fat matter obtained by the evaporation of the ethereous tinctures is of an orange-yellow colour. The first tinctures afforded a fat matter more coloured and reddish, proceeding from a certain quantity of carminium, which the fat matter had taken up. This fat matter has the smell of decoctions of cochineal. By dissolving it in hot absolute alcohol, there was obtained, on cooling, a large quantity of a pearly crystalline matter, of a rose-white colour, sprinkled with red points. By repeated solutions and crystallizations, it was rendered colourless; nor did it retain either taste or smell. Insoluble in water and cold alcohol, it dissolved in ether, fused at a heat of 40° Cent. (104° Fahr.) and formed with alkalies well characterized soaps. This substance is therefore a fat, translucent, crystallizable, similar to what M. Chevreul has found in the fats of mammifera, and which he has called *stearine*. In cochineal, a little *elaine* is associated with it, which is obtained by evaporating off the alcohol.

The pretended yellow colouring matter of cochineal, of which mention is made in some books, does not exist. Fat matter, loaded with carminium, has been mistaken for it; for carminium affords yellow solutions, when it contains a fat matter in a pretty large proportion. Carminium even possesses the property of rendering the fat matter soluble in water. In fact, if we treat cochineal with boiling alcohol, without having exposed it previously to ether, we obtain a kind of crystals similar to what are mentioned in the beginning of this memoir, but much more loaded with fat matter. These crystals do not readily dissolve in water, and the solution is of an orange yellow approaching to red. When treated by the methods above pointed out, they are found to be composed of carminium and fat matter in a very large proportion; and though entirely soluble in water, they retain still a little animal matter.

By incinerating cochineal, certain salts were found in the residue. Hence the general products are as follows:—

1. Carminium. 2. A peculiar animal matter. 3. A fat matter, containing stearine, elaine, and odorant principle. 4. Salts, phosphate of lime, carbonate of lime, muriate of potash, phosphate of potash, potash united to an organic acid.

#### SECOND PART.—Of *Cochineal* in reference to its employment in the Arts.

All the acids form precipitates in the watery decoction of cochineal, but these precipitates are stronger in proportion to the abundance of the animal matter; hence they do not appear, or only after a certain time, when the boiling is slight, or the decoction too much diluted. The precipitates are generally of a pretty fine colour; but the shade varies according to

the acid employed, and its quantity. The acidulous salts, such as the bitartrate and bioxalate of potash, also produce precipitates in the decoction of cochineal. The alkalies change the colour to crimson without causing any precipitate; they even redissolve the precipitates occasioned by the acids.

If we add to water in which cochineal is to be boiled a certain quantity of alkali, there is then dissolved a much larger quantity of the animal matter; and when we thereafter add some acid, a much more abundant precipitate takes place. These precipitates are commonly of a beautiful red. By drying they take so deep a colour as to appear brown; but on diffusion through water, they recover their brightness. The alkali appears to act in the decoction, not only as a solvent of the animal matter, but likewise by modifying the colouring matter. These precipitates are perfectly pure carmines. The neutral alkaline salts, and most of the metallic, act on this decoction as on the solution of carmine.

It has been remarked, that the decoction of cochineal can be kept a long time without alteration. It is known that carminium cannot pass into a putrid fermentation, but the animal matter is very easily decomposed. This, however, in the decoction of cochineal, seems to be preserved from change by its union with the colouring matter.

#### *On Carmine and Carminated Lakes.*

The process followed in Germany for making carmine, which consists in pouring a certain quantity of solution of alum into a decoction of cochineal, is the most simple of all, and affords an explanation of the formation of carmine, which is merely the carminium and the animal matter precipitated by the excess of acid in the salt, which has taken down with it a small quantity of alumina; but it appears that alumina ought not to be regarded as essential to the formation of carmine. In fact, by another process, called by the name of Madame Cenette, of Amsterdam, the carmine is thrown down by pouring into the decoction of cochineal a certain quantity of binoxalate of potash. When carbonate of soda is added, then carminated lake also falls down. That carmine is a triple compound of animal matter, carminium, and an acid, appears from the circumstance that liquors which have afforded their carmine, when a somewhat strong acid is poured into them, yield a new formation of carmine by the precipitation of the last portions of the animal matter. But whenever the whole animal matter is thrown down, the decoctions, although still much charged with the colouring principle, can afford no more carmine. Such decoctions may be usefully employed to make carminated lakes, saturating the acid with a slight excess of alkali, and adding gelatinous alumina. The precipitates obtained on adding acids to the alkaline decoctions of cochineal, are there-

fore true carmines, since they do not contain alumina ; but the small quantity of alumina which is thrown down by alum in the manufacture of carmine, augments its bulk and weight. It gives besides a greater lustre to the colour, even from diluting and weakening it a little.

The carmines found in the shops of Paris were analyzed, and yielded the same products. They decomposed by the action of heat, with the diffusion at first of a very strong smell of burning animal matter, and then of sulphur. A white powder remained, amounting to about one-tenth of the matter employed, and which was found to be alumina. Other quantities of carmine were treated with a solution of caustic potash, which completely dissolved them, with the exception of a beautiful red powder, not acted on by potash and concentrated acids, and which was recognized to be red sulphuret of mercury, or vermilion. This matter, evidently foreign to the carmine, appears to have been added, in order to increase its weight.

The preceding observations and experiments seem calculated to throw some light on the art of dyeing scarlet and crimson. The former is effected by employing a cochineal bath, to which there have been added, in determinate proportions, bitartrate of potash and permuriate of tin. The effect of these two salts is now well known. The former, in consequence of its excess of acid, tends to redden the colour, and to precipitate it along with the animal matter : the latter acts in the same manner, at first by its excess of acid, then by the oxyde of tin which falls down also with the carmine and animal matter, and is fixed on the wool, with which it has of itself a strong tendency to combine. MM. Pelletier and Caven-tou remark, that "to obtain a beautiful shade, the muriate of tin ought to be entirely at the maximum of oxydizement ; and it is in reality in this state that it must exist in the solution of tin prepared according to the proportions prescribed in M. Berthollet's treatise on dyeing."

We hence see why, in dyeing scarlet, the employment of alum is carefully avoided, as this salt tends to convert the shade to crimson. The presence of an alkali would seem less to be feared. The alkali would occasion, no doubt, a crimson-coloured bath ; but it would be easy in this case to restore the colour by using a larger quantity of tartar. We should, therefore, procure the advantage of having a bath better charged with colouring matter and animal substance. It is for experience on the large scale to determine this point. As to the earthy salts, they must be carefully avoided ; and if the waters be selenitish, it would be a reason for adding a little alkali.

To obtain crimson, it is sufficient, as we know, to add alum to the cochineal bath, or to boil the scarlet cloth in alum water. It is also proper to diminish the dose of the salt of tin, since it is found to counteract the action of the alum.

The alkalies ought to be rejected as a means of changing scarlet to crimson. In fact, crimsons prepared by this process cannot be permanent colours, as they pass into reds by the action of acids.

NOTE LL. p. 347.

According to M. Von Grotthuss, carmine may be deprived of its golden shade by ammonia, and subsequent treatment with acetic acid and alcohol. Since this fact was made known, M. Herschell, colour-maker, at Halle, has prepared a most beautiful carmine.

NOTE MM. p. 361.

*Chemical examination of Kermes (coccus ilicis) by J. L. Lassaigne.*

On applying to these insects the processes employed by MM. Pelletier and Caventou in the analysis of cochineal, M. Lassaigne obtained analogous results.

Kermes, treated with boiling sulphuric ether, yielded a yellow fat matter, which may be obtained in an insulated state by evaporation of the solvent; and a little of its red colouring matter may be carried off by digesting it in cold alcohol of 30° Baumé (sp. gr. 868.) This fat substance is inodorous, of a slightly styptic taste, without action on litmus infusion, fusible at 45° Cent. (113° Fahr.), and easily saponified by alkalies.

Kermes, exhausted by ether, yields to alcohol, by means of heat, a colouring matter and a brown animal matter. On cooling, the latter is precipitated in reddish flocks, mingled with the colouring matter carried off by the alcohol. The alcoholic solutions, when evaporated in a glass retort, leave the colouring matter of kermes; but to procure it perfectly pure, it must be several times redissolved in alcohol.

This matter has a very deep purple red colour. It has a granular aspect and crystalline fracture. The air has no action on it. Its powder possesses a beautiful vermilion hue.

Sulphuric ether does not affect its solution; but water and alcohol dissolve it in any proportion. The more concentrated the latter is, however, the less is its solvent faculty. Reagents affect this matter like carminium, to which it bears a close resemblance.

Kermes, after having been treated successively by ether and alcohol, remains a little coloured. On boiling it with water, the last portions of colouring matter may be removed, and there remains a brownish animal matter, in semitransparent scales, very slightly soluble in water, and possessing all the properties of the animal matter of the cochineal.

It hence appears, that kermes has a chemical composition, very analogous to that of cochineal.—*Annales de chimie et physique*, xii. 102.

## NOTE NN. p. 364.

SEED-LAC is obtained in the following manner. When the lac has been separated from the stems (sticks) to which it naturally adheres, and is reduced to a coarse powder, the silk and cotton dyers extract its colours as much as they can by means of water; and to the hard and yellowish resinous powder which remains, and which resembles in some measure mustard-seed, the name of *seed-lac* is given.

Shell-lac is procured by melting seed-lac in a cotton bag, above a glowing charcoal fire: when the lac is melted, it is forced through the bag by twisting it, and is received on the smooth trunk of a tree. The resin being the most fusible portion of the lac, passes through the bag in a state of great purity.

The lac-lake contains, besides the colouring matter of the lac, about a third of its weight of resin, a sixth of alumina, and much earthy matter.

Mr. Bancroft has given a full account of the mode of preparing lac-lake. Lac-lake is prepared in India, from stick-lac reduced to powder, by repeated affusions of boiling water containing a large quantity of soda; but this addition of soda, although it disposes the water to extract the colouring portion of the lac much more copiously, occasions a considerable solution of resin, which is afterwards precipitated, intimately combined with the colouring principle, by the alum employed in its precipitation. Hence the lac-lake, besides its colouring matter, contains, as previously stated, different proportions of resin and alumina. The proportion of resin may be estimated at one-third of its weight, and that of alumina at one-sixth. It contains, likewise, a portion of vegetable matter derived from the mucilaginous bark of an Indian tree called *lodu*, which is supposed to be useful in several respects. But this point has not been hitherto decided. Considerable but variable proportions of sand, and other earthy matters, are usually added to the lac-lake by the manufacturers to increase its weight.

The lac-lake, after being ground to a fine powder in proper mills, is put into wooden troughs with water, where it settles, and the colourless supernatant liquor is drawn off. The sediment or moistened powder must then be put into a leaden cistern, where it is diffused through dilute sulphuric acid, whereby a limpid solution of the colouring matter is obtained. Thus it is separated from the foreign substances, resinous or earthy, and rendered capable of application to stuffs. Sulphuric acid possesses the property of destroying the bad effects of the resin much better than the muriatic.

For dissolving the colouring matter in this way, three pounds of oil of vitriol, specific gravity 1.845, (169° Tw.) are required for every four pounds of the dry lac-lake before it was milled. The ground and moist lac-lake should not contain more than twice its weight of water. The sulphuric acid is in that case added, and perfectly mixed with the moist



powder, stirring up and agitating with a strong rod or ladle of glass or lead. But if the lac-lake has been ground without being moistened, it will be proper, before adding the acid, to dilute this with twice its weight of water. When the preceding mixture is made, it must be left in repose for twenty-four hours in summer, and forty-eight in winter. Then a gallon of boiling water must be added for every pound of lac-lake (weighed dry,) and the whole must be well mixed. After leaving the mixture at rest for twenty-four hours, the limpid coloured solution ought to be drawn off into another leaden vessel, and the same quantity of boiling water poured upon the residuum. This mixture, after being well stirred, is to be left at rest for twelve hours as before, and then the clear liquor may be drawn off. The same quantity of boiling water may be again thrown on the residuum, which after repose is to be separated. This treatment is to be repeated as long as boiling water acquires colour. When this ceases, a little of the residuum is to be mixed with one-half its weight of carbonate of soda dissolved in a little water, and if the whole colouring matter has not been extracted, it will become red, and will deepen in colour. If after this trial there should seem to remain a quantity of colour worthy the trouble of extraction, the residuum should be mixed with from one-sixth to one-fourth of the quantity of sulphuric acid primitively employed, and after leaving the mixture at rest for twelve hours, boiling water is to be poured on it as above directed. This operation may be resumed till the whole of the colouring matter has been extracted.

The coloured liquid being now all collected in the same vessel, there must be very exactly mixed into it two pounds of pure lime, well calcined and reduced to a fine powder, for every five pounds of sulphuric acid contained in the liquor. This quantity of lime will be sufficient to neutralize four-fifths of the acid, and to carry it down (in the form of sulphate of lime) without any colouring matter. The supernatant liquid is then to be decanted, and the remaining fifth of acid which it contains disposes the colouring matter contained in the liquor better to penetrate and impregnate the stuff. This liquor or solution of lac colour, may be called No. 1. This may be employed without any difficulty in dyeing, as if it were a weak decoction of cochineal, along with the mordants and other acids to be presently described. We shall merely observe at present that two-thirds of the sulphuric acid prescribed for the lac-lake will be sufficient for extracting the colour of the lac-dye; but although neither the labour nor the expense of extracting the colouring matter of either of these substances be considerable, it is probable that the greater number of dyers will deem it sufficient to subject the lac-lake or the lac-dye to the action of sulphuric acid, so as to deprive the resinous portions of their adhesive property: in this case, the colouring matter becomes soluble in the dyeing liquor, and may be applied to the stuff, without any previous

separation of the resinous and other matters soluble in these preparations. For this purpose, one pound of sulphuric acid at most, should be employed for every two pounds of lac-lake weighed in its dry condition ; two-thirds of a pound will be sufficient for two pounds of the lac-dye. Each of these substances being moistened and milled, as we have already explained, ought to be mixed in a leaden vessel with the determinate proportion of sulphuric acid. After having stirred them well at different times, the mixture must be left at rest for at least twenty-four hours in summer, and thrice this time in winter. After this, it will be proper to employ it immediately in the manner to be presently pointed out. The cost of the preparation may be estimated at 20 per cent, independent of the expense of grinding. This preparation of lac-lake or the lac dye, may be called No. 2.

From two to three pounds of lac-lake, according to the quality, and perhaps a little less of the lac dye, can produce the effect of a pound of cochineal ; but to give the greatest vivacity to the colour, a sixth or an eighth of nitromuriate or other solution of tin, must be used in the dyeing more than is employed with cochineal, because the alumina, by which the colour of the lac was at first precipitated, and of which a portion has been redissolved and retained by the sulphuric acid, and in the operation just described, would give to the colour a crimson tint, unless the oxyde of tin be employed in such quantity as to repel, by its superior attraction, (affinity), the alumina, and prevent it from becoming attached to the stuff and to the colouring matter.

It is admitted that the colour extracted from the lac resists the action of acids much better than cochineal. Besides this advantage, the scarlet colour may be obtained better and cheaper with this substance at a single operation. For this purpose, we must put into a vessel of block tin a sufficient quantity of clear soft water, to which we add one pound of tartar, or, which is better, powdered cream of tartar, for every ten pounds of stuff, with as much either of quercitron bark in powder, contained in a bag, or otherwise fustet (*rhhus cotinus*) in chips, also enclosed in a bag. These ingredients will produce abundance of the yellow colour. Having raised this composition to the boiling point, we must add nitro-muriate of tin, or any other solution of this metal, with a suitable quantity of the colour of lac-lake No. 1. or of that of No. 2. This mixture being thoroughly made, the stuff, previously cleaned and moistened, is to be thrown into the bath, and turned through it by a winch, as is usually practised, till it has acquired sufficient body and brilliancy of colour. This commonly takes place in an hour, if the liquor be kept constantly boiling. To prevent any chance of imperfection in the dye, a little more lac colour should be used for each operation, since the superfluity will serve, without any loss, for the other pieces of stuff which are to be dyed in the sequel.

If it be judged proper to neutralize a portion of the sulphuric acid employed in preparing No. 2, to prevent the harshness which the acids are supposed to give to goods, this may be done by the addition from time to time of carbonate of soda, not exceeding a pound, or a pound and a half, for every pound of sulphuric acid that was employed.

If one-fourth part of the solution No. 1, or of the preparation No. 2, be kept out, and there be added, towards the end of the process, a quarter of an ounce of cochineal for every pound of stuff to be dyed, we shall obtain a colour equal in vivacity and beauty to scarlet dyed entirely with cochineal.

When a stuff is dyed with the lac-lake on purpose to change its shade afterwards to a bright rose, to a crimson or purple, neither quercitron nor fustet should be used, nor more than half the quantity of tartar. The stuff dyed without these ingredients is to be thereafter washed, and put into a clean vessel, along with warm water, containing a moderate portion of carbonate of soda in solution of ammonia. If a more decided purple be wanted, we must add a little archil to the bath, or alkaline liquor, and then proceed as usual. But as the colour of archil is not sufficiently permanent, dyes partaking more or less of the purple, moderately beautiful and fast, may be obtained directly, by adding to the bath composed of No. 1. or No. 2, a suitable proportion of a decoction of logwood. This addition need not, however, be made before the end of the operation ; and when logwood is to be used, neither fustet nor quercitron are needed ; but as tartar renders the colour of logwood more durable, it becomes necessary, and the solution of tin is indispensable. We must, however, beware of turning the stuff with the winch in the bath, before the logwood be added, and thoroughly mixed with the liquor.

If a stuff be dyed with one of the preparations No. 1 or No 2 if pulverized quicklime in sufficient quantity to neutralize the acid be added to the bath ; and if the boiling be kept up for a quarter of an hour, a good crimson may be obtained without any solution of tin, or other ingredients, that are required for scarlet. In this case, the alumina re-dissolved by the sulphuric acid, and the sulphate of lime, serve for mordants.

Mr. Hatchett, in his admirable memoir on lac, published in the Philosophical Transactions for 1804, states the composition of stick-lac to be,

Colouring extract . . . . .	20
Resin . . . . .	136
Vegetable gluten . . . . .	11
Wax, with a little colouring extract . . . . .	12
Extraneous substances . . . . .	13
	<hr/>
	192
Loss . . . . .	8
	<hr/>
	200

200 grains of seed-lac yielded him only .	5 of colouring matter.
500 „ shell-lac . . . . .	2.5 „ „
	454.5 resin.

Mr. Hatchett in that memoir states, that the colouring extract of lac is insoluble in ether, scarcely soluble in alcohol, and slightly so in water, but readily in sulphuric acid, forming a deep brownish-red solution, which being diluted with water, and saturated with potash, soda, or ammonia, becomes changed to a deep reddish purple. Strong acetic acid dissolves it with great ease, and forms a deep brownish-red solution. The lixivia of potash, soda, and ammonia, act powerfully on this substance, and almost immediately form perfect solutions, of a beautiful deep purple colour. Pure alumina put into the aqueous solution does not immediately produce any effect; but upon the addition of a few drops of muriatic acid, the colouring matter speedily combines with the alumina, and a beautiful lake is formed. Mr. Bancroft states, that muriatic acid does not answer so well as sulphuric, in preparing the lac dye.

Muriate of tin, says Mr. Hatchett, produces a fine crimson precipitate, when added to the aqueous solution. A similar coloured precipitate is also formed by the addition of solution of isinglass. Probably the tannin thus indicated was afforded by the small portions of vegetable bodies, from which the stick-lac can seldom be completely separated.

Twenty grains of borax, dissolved in 4 ounces of water, form a liquid capable of dissolving 100 grains of shell-lac. This solution of lac in water, mixed with various colours, as vermilion, fine lake, indigo, prussian blue, sap-green, or gamboge, forms an excellent vehicle for their application to paper, since, when it dries, the colour cannot be removed with a moistened sponge. The Indians make an ink by mixing the above vehicle with lamp-black.

#### NOTE OO. p. 379.

M. P. A. de Bonsdorff has pointed out several new applications of brazil wood as a chemical re-agent. It may enable us to distinguish one acid from another. Sulphuric acid concentrated, or diluted with three parts of water, instantly gives to paper stained with brazil wood a bright rose colour, which, attracting humidity from the air, gradually passes to orange. More dilute it gives a dirty yellow. Nitric and muriatic acids act like the sulphuric. Sulphurous acid gas blanches the colour. Concentrated dydriodic acid yields a rose colour, which becomes first yellow on the edges, and finally throughout. Diluted acid gives a fading yellow. Fluoric acid, or fluosillicic, causes a clear red colour. Diluted, it instantly produces a fine lemon-yellow colour, which in the space of a minute disappears, and soon leaves a tint of greenish-grey, which, observed by transmitted light, is of an olive-green. When exposed to the gaseous acid, the paper passes

through these transitions of colour, a phenomenon which does not occur with the other acid vapours. Fluboric acid has the same habitudes. Boracic acid does not act at first, but by and by the colour of the paper becomes pale, and ends in a white, bordering a very little on red. If boracic contain traces of the sulphuric, a marked yellowish colour is formed, which soon disappears. Concentrated phosphoric acid gives a rose colour, which, in the air, slowly changes to orange. Dilute, it yields a permanent yellow. Hypophosphorous gives a red, which passes through yellow to white. Concentrated arsenic acid produces a pretty durable rose colour; diluted, a fugitive yellow. Arsenious acid has no sensible effect. Concentrated acetic acid gives instantly a sombre yellowish colour, which immediately disappears, and is succeeded by a pale violet colour, which, viewed by transmitted light, is a very deep violet-red; diluted, a yellowish colour, becoming violet-red. When this acid is mixed with the sulphuric, a yellowish colour appears, instead of violet red. Acetic acid, containing no more than  $\frac{1}{10}$  part of sulphuric, affords a very perceptible yellowish colour. Citric acid, a beautiful permanent yellow. Tartaric and malic acids, a yellow becoming dirty. Concentrated oxalic acid, an orange colour, becoming slowly yellow; diluted, a durable yellow.

Woollen cloth, plunged into a boiling bath of brazil wood, then drained, and dipped for some minutes in a dilute phosphoric or citric acid, or what is cheaper and equally good, in a dilute bisulphate of lime, takes a very lively yellow dye, which resists washing with soap. Silk may be dyed by the same process, but cotton or linen cannot.

The bright fugitive red, called fancy-red, is given to cotton by Nicaragua, or peach wood, a cheap kind of brazil wood.

The cotton being scoured and bleached, is boiled with sumach. It is then impregnated with a solution of tin (at 5° Baumé, 6 $\frac{3}{4}$ ° Tw., according to Vitalis.) It should now be washed slightly in a weak bath of the dyeing wood, and lastly worked in a somewhat stale infusion of the peach or brazil wood. When the temperature of this is lukewarm, the dye is said to take better. Sometimes two successive immersions in the bath are given. It is now wrung out, aired, washed in water, and dried.

M. Vitalis says, that his solution of tin is prepared with two ounces of tin, and a pound of aqua regia made with two parts of nitric acid at 24° Baumé, (40° Tw.) and three parts of muriatic acid at 22° (36° Tw.)

For a *rose* colour, the cotton is alumed as usual, and washed from the alum. It then gets the tin mordant, and is again washed. It is now turned through the dye-bath—an operation which is repeated if necessary.

For *purple*, a little alum is added to the brazil bath.

For *amaranth*, the cotton is strongly galled, dried, and washed. 2. It is passed through acetate of iron, till it has taken a strong grey shade.

3. It receives a bath of lime-water. 4. Mordant of tin. 5. Dyeing in the brazil wood bath. 6. The two last operations are repeated.

The following example of a spirit red, directly applied in calico printing, is given in Rees' Cyclopædia, article COLOUR :—

Prepare an aqua regia, by dissolving two ounces of sal ammoniac in one pound of nitrous acid, sp. gravity 1.25. (25° Tw.) To this add two ounces of fine grain tin; decant it carefully off the sediment, and dilute it with one-fourth its weight of pure or distilled water.

To one gallon of water add one pound of cochineal, ground as fine as flour; boil half an hour; then add two ounces of finely pulverized gum dragon (*tragacanth*), and two ounces of cream of tartar, and stir the whole till it is dissolved. When the liquor is cool, add one measure of the preceding solution of tin to two of the cochineal liquor, and incorporate well by stirring. Apply this with the pencil or block; suffer it to remain on the cloth six or eight hours; then rinse off in spring water. This colour will be a bright and beautiful scarlet.

2. Boil twelve pounds of brazil chips during an hour, in as much water as will cover them. Draw off the decoction, pour on fresh water, and boil as before. Add the two liquors together, and evaporate slowly down to one gallon. To the decoction, while warm, add four ounces of sal ammoniac, and as much gum dragon, or senegal, as will thicken it for the work required. When cool, add one of the solution of tin above described to four, six, or eight of the brazil liquor, according to the colour wanted. Suffer it to remain for eighteen or twenty hours on the cloth; then rinse off in spring water as before. The colour will be a pale and delicate pink. If it be required deeper, the decoction must be made stronger, and used in the proportion of three or four to one of the solution of tin. Nicaragua or peach wood, though not so rich in colouring matter as brazil, yields a colour, however, which is, if possible, more delicate and beautiful.

#### NOTE PP. p. 384.

DR. DINGLER, manufacturing chemist at Augsburg, gives the following prescription for dyeing with brazil woods of inferior qualities, and clearing these dyes of their tawny pigment. The watery infusions of these poorer dyewoods are to be evaporated till from four parts of wood by weight there remain only 12 or 15 of liquid. When this liquid has cooled, we must pour into it, after twelve or eighteen hours, two parts of skimmed milk. After stirring this mixtures well, we boil it for a few minutes; then pass it through a thick piece of flannel. The tawny colour will be then seen to attach itself to the caseous part of the milk, which spontaneously precipitates from this decoction, without occasioning the least loss in the quantity of red colour. The remaining red is of a pure tint. Perhaps this process

might be useful with madders, which are supposed to consist of the same two colours. Two pounds of milk are sufficient for six or eight pounds of young woods.

NOTE QQ. p. 387.

THE colouring principle of logwood was discovered by M. Chevreul, and called *Hematin*.

Ground logwood is to be digested in water at a temperature of from 120° to 130° Fahr. After a few hours the liquor is filtered and evaporated to dryness. The residuum is put into alcohol of 36° Baumé, (sp. gr. 837) for a day. After this he filters the new liquor, concentrates it till it thickens, pours into it a little water, exposes it anew to a gentle evaporation, and then leaves it to itself. By this means he obtains a pretty large quantity of crystals of *hematin*, which, to be rendered pure, need only be washed in alcohol and dried.

This substance is crystalline of a rosy-white, very brilliant when viewed through a lens, having a taste slightly astringent, bitter, and acrid.

Exposed to the action of fire in a retort, hematin affords all the products of animal substances, and, besides, a small quantity of ammonia, which proves that it contains azote.

Boiling water dissolves it easily, taking an orange-red colour, which passes to yellow by cooling, but which may be restored by heating the solution anew. When this is evaporated, crystals of hematin are formed. On adding to it some acid very gradually, it changes to yellow and then to red. Sulphurous acid yellows and then blanches the colour.

Potash and ammonia cause the solution of hematin to take a purple red; if a great excess of these alkalies be added, the colour becomes violet-blue, then brown-red, and finally yellow-brown. The hematin is now decomposed; it cannot be recovered by acids.

If a current of sulphuretted hydrogen gas be passed through water charged with hematin it takes a yellow colour, which vanishes after a few days. The sulphuretted hydrogen appears to act by combining with the hematin, and not by deoxydizing it. This is easily verified by putting into a small jar, filled with mercury, a certain quantity of the blanched solution, and then introducing a bit of pure potash. This melts, combines with the sulphuretted hydrogen, and the colour of the hematin immediately reappears.

Protoxide of lead, protoxide of tin, hydrate of tritoxide of iron, hydrate of copper, hydrate of nickel, oxyde of zinc and its hydrate, flowers of antimony, oxyde of bismuth, combine with hematin, and give it a blue colour, with a loss of the violet shade. The deutoxyde of tin acts on it in the manner of the mineral acids.

Hematin precipitates glue from its solution, under the form of reddish flocks.

M. Chevreul proposes it as a good re-agent for acids.—*Annales de Chimie*, vol. lxxxi. p. 128.

NOTE RR. p. 402.

DR. JOHN, of Berlin, gives the following as the results of his examination of annotto. The grains of Rocou contain an aroma, an acid, resin combined with the colouring matter, vegetable mucilage, fibrin, coloured extractive, and a peculiar matter which approaches to mucilage and extractive. This analysis explains the reason why an alkali is added to annotto when it is employed in dyeing. The alkali combines with the resin, and forms a soap which dissolves in water. The alkali acts likewise on the colouring matter, and renders it more lively.

NOTE SS. p. 408.

THE application to stuffs of colours derived from the mineral kingdom, is one of the most marked improvements in modern dyeing. Mr. Raymond received from the French government, in 1811, 8000 francs, as a reward for communicating to the public his process for dyeing silk of a uniform, fast, and bright prussian blue colour.

By a gentle calcination till sulphurous acid fumes begin to appear, he first converts copperas into the red sulphate of iron. This he dissolves in sixteen times its weight of warm water, and filters, when he has a clear solution of a lively yellow colour, bordering on red. The silk, prepared as for the indigo dye, is to be put into the solution of iron, and left there a shorter or longer time, according to the shade of blue that is wanted. It is then taken out of the vat, and wrung very dry over a pole placed over the vat. The silk is next carried to the stream, to be thoroughly cleansed, which is effected by twice beetling it, and plunging and agitating it each time in the running water. The water now wrung out of the silk should not be able to affect solution of ferroprussiate of potash. An ounce of green copperas will furnish red sulphate sufficient for a pound of water. Dissolve in pure water, heated to 60° Reaumur, (167° Fahr.,) and put into a deal vat, or tub, one ounce of ferroprussiate of potash for every twelve ounces of silk to be dyed. When the prussiate is entirely dissolved, add one ounce, or even rather more, of muriatic acid, at about 21° Baumé, (34° Tw.,) stirring the mixture well. When the liquor has acquired a greenish colour, the silk must be immediately plunged in it, and stirred about for some minutes, after it has been well wrung and disposed upon poles, in the same manner as for the iron mordant.

The silk having received in an equal manner the dye of prussian blue, it is taken out of the prussiate vat, and after being well wrung on a pole above the vat, it is taken to the river, where it must receive two or three beetlings, and must be plunged and agitated each time in the water, (in



the same manner as for dyeing black,) in order to free it entirely from any portion of prussiate of iron that is not truly combined in it, and which, by remaining partly interposed in the silk, would cause it to dye the water blue, and also to produce stains of blue on any white body on which it is rubbed. 50° Reaumur (144° Fahr.) is the most suitable temperature for the prussiate bath. Should the bath of prussiate of potash become of a blue colour, when the silk is dipped into it, it is an indication that it contains either too much prussiate or muriatic acid, or that the silk, after passing through the mordant of oxyde of iron, had not been sufficiently cleansed in the river.

Lastly, the silk being well washed in the stream, and thoroughly wrung with the hands, is to be placed loosely on the poles, as in the preceding operations; after which it must be well stirred and agitated in a large vessel, three-fourths filled with cold water, and to which must be added, for a hundred pounds of silk, two pounds of ammonia, (water of,) marking 21° of Baumé's spirit hydrometer (sp. gr. 922.) The blue colour will immediately become at least three shades deeper, taking a much richer and brighter tint, at the same time fixing more perfectly in the silk. This change is effected in a few minutes. The silk must then be wrung by hand, and rinsed in running water without beating. After this it is dried on the poles, in the same manner as other dyed silks. It need be left on the poles only twenty hours, to give the colour time to come out well; for it is observed, that this colour, far from fading in the drying, as is the case with many other colours, is improved, and acquires a greater richness of tint. The solution of a little soap added cold to the ammonia bath improves it, giving also softness to the silk, and rendering it more easy to separate. The soap must be uniformly dissolved.

Woollen cloth takes the above dye, but it must be left longer than silk in the iron mordant.

In 1819, M. Braconnot, of Nancy, applied sulphuret of arsenic (opiment) to stuffs, so as to give them a yellow dye. He mixed one part of sulphur, two parts of arsenious acid, and five parts of potash of commerce. This mixture is fused in a crucible, at a heat approaching to redness. The resulting yellow mass is to be dissolved in hot water; and the liquor is filtered to separate it from a sediment formed in a great measure of metallic arsenic in brilliant scales, and of a small quantity of a flocky chocolate-coloured matter, apparently a subsulphuret of arsenic. Into the filtered liquor, diluted with water, weak sulphuric acid is to be poured, which causes a flocky precipitate of a superb yellow colour. This precipitate, washed in a cloth, dissolves with extreme readiness in water of ammonia, constituting a yellowish liquid, into which an excess of ammonia is poured to deprive it entirely of colour. In this liquor, the wool, silk, cotton, or linen to be dyed, is plunged; and it may be diluted to any degree, cor-

responding to the depth of shade wanted. The washed sulphuret of arsenic should be dissolved in ammonia only when it is wanted ; and metallic vessels or utensils should be carefully avoided. When the stuffs are taken out of this bath, they are colourless ; but they imperceptibly assume a yellow colour on the dissipation of the ammonia. They are, therefore, freely exposed to the air, so that it may play over their surfaces ; and as soon as the colour has taken its utmost intensity of shade, they may be washed and dried.

Wool should be tramped in the ammoniacal bath till it is uniformly impregnated with it ; it is then to be squeezed or wrung out very slightly and uniformly, or it may be even allowed simply to drain. Silk, cotton, hemp, linen, require merely to be dipped in the dyeing liquor. They are very easily impregnated, and must be well wrung out. This colour is affected only by alkalies. It may be had of every shade, from golden yellows to the palest.—*Annales de Chim. et de Phys.* xii. 398.

M. J. L. Lassaigne, in 1820, published, in the *Annales de Chimie et de Physique*, a process for fixing chromate of lead on cloths, which has since become pretty common in this country. After immersing for a quarter of an hour, at the ordinary temperature, hanks of scoured silk in a weak solution of acetate of lead, he took them out and washed them with a great deal of water. Thus prepared, they were dipped into a weak solution of chromate of potash. They immediately took a fine yellow colour, and at the end of ten minutes the effect was completed. From this colour being decomposed in part by soap water, M. Lassaigne conceives that it will be chiefly applicable to silks. But by applying a mordant of acetate or nitrate of lead, and passing the goods through bichromate of potash, a very beautiful and sufficiently fast yellow is now given to cotton goods in this country. The bichromate acts instantly the mordant, and does not require that duration of immersion which M. Lassaigne found to be necessary with the neutral chromate.

The application of the chromate of lead on Turkey red cloth forms a brilliant style of calico printing, now carried on to high perfection at the establishment of Messrs. Monteith, at Glasgow. Nitrate of lead is dissolved in liquid tartaric acid, of a specific gravity about 1.250 ; this solution is thickened with gum, and applied with the block to cloth previously dyed Turkey red. Whenever the paste is dried, the cloth is slowly passed through an aqueous solution, nearly saturated, of chloride of lime, kept at the temperature of about 100° in a stone trough. The tartaric acid disengaging the chlorine, discharges the colour of the Turkey red at points of application, while the nitrate of lead, or rather, perhaps, the oxyde of lead, remains attached to the cloth. This is immediately washed, and then passed through a solution of bichromate of potash, by means of the padding machine.

An orange colour was some time ago given to goods, in calico printing, by means of the crystals of hydrosulphuret of soda and antimony, which are hence called orange crystals. But the use of the alkaline solution of sulphuret of antimony had been long known and practised by the Lancashire printers. It was invented by Mr. John Mercer, at Messrs. Fort's. The salt is formed by boiling finely ground sulphuret of antimony in caustic soda ley, and crystallizing.

The thickened solution of the hydrosulphet is applied to the cloth, and it is either washed off in weak sulphuric acid, or in water, after being left some days on the cloth. This dye is bright and pleasing, but very fugitive, and has hence gone into disuse.

For the following observations on calico printing, I am indebted to a much esteemed friend, who unites scientific knowledge to practical skill.

*Bleaching.*—To bleach cloth for printing, it is first of all to be singed, and then steeped in warm water (sometimes with an addition of spent ley) for a day or two. It is then well washed and boiled in potash ley five different times.

For 2000lbs. (original weight) of cloth, 1000 gallons of water, and 40 to 45lbs. of potash are employed each time. The boiling is continued eight or ten hours.

Between each operation the cloth must be well washed, and after the third and fourth boil it must be spread upon the grass, or steeped for a night in a weak solution of chloride of lime. After this, it is winced a few minutes in a warm dilute sulphuric acid, well washed and dried.

The principal processes, or rather styles of work, as they are called, are the following :—

1. Single coloured plates.
2. Ditto ditto grounded.
3. Light or dark chintzes.
4. Dark grounds, with a white discharge.
5. Blue grounds, with a white resist.
6. Blue grounds, with a red and white resist together.
7. Chemical or spirit colours.

1. *Single Colours.*—Called plates, from their being generally printed with the copper-plate. This process consists generally in printing a mordant upon the cloth; which mordant attracts a colouring matter when the cloth is dyed. The mordant is different, according to the colour that is wanted.

For *black*. An acetate of iron is used of the sp. gr. 1.040.

For *purple*. An acetate of iron, sp. gr. 1.12, with six, eight, or twelve times its volume of water, according to the shade of colour required, and the mass to be printed.

For *red*. A solution of three pounds alum in a gallon of water, one-half of which is decomposed by acetate of lime or lead.

For *chocolate*. Mixtures of acetate of iron, sp. gr. 1.12, with red mordant, in the proportions of one to two, four, six, according to the shade.

Each of these mordants is thickened with flour, or, in some cases, with gum, and printed upon the bleached cloth.

After being exposed to the air for a few days in a warm room, the goods are taken down and passed through the dung copper, at a heat of from 150° to that of boiling water. They are then washed, and winced in another clean dung copper, at a lower degree of heat than before, and then washed again. They are now ready to be dyed.

All the colours last mentioned, viz. black, purple, red, and chocolate, are dyed with madder and sumach, except purple, in which the sumach is omitted. Different quantities of madder are used, according to the quantity of colour on the cloth, from one pound per piece of 21 square yards, to three and even three and a half pounds; the sumach about one-eighth of the madder. The goods are *entered* when the copper is cool, and the heat is brought up gradually during two or three hours, and sometimes the ebullition is kept up for a quarter of an hour; the pieces all the while being turned over a wince, from the one side of the copper vessel to the other. They are then washed, and boiled in bran and water ten or fifteen minutes.

If they have much white, they must be *branned* a second and a third time, washing between each operation.

To complete the whitening, they are spread upon the grass for a few days; or what is more expeditious, and more generally practised now, they are winced a short time in a warm but weak solution of chloride of lime.

For *indigo blue*. A strong solution of caustic potash is made, in every gallon of which, by the aid of as much orpiment, twelve or sixteen ounces of good indigo is dissolved. The solution, when clear, is thickened with gum. This being printed upon the cloth, nothing more is necessary than to wash it when dry.

For *prussian blue*. The same mordant is used as for black; but after cleansing, the piece is winced in a solution of prussiate of potash, in which the prussic acid has been set free by means of sulphuric acid.

For *gold*. Five pounds sulphate of iron, and one and a half pounds acetate of lead are dissolved in a gallon of water: the solution, thickened with gum, is printed on the cloth; and, after eight or ten days' age, is winced in a solution of potash made thick with lime. As soon as the black oxyde of iron, which is precipitated, commences to redden, the piece is removed to a vessel of water, and then washed.

2. *Single colours grounded*.—A second, and sometimes third colour, is

grounded or printed in with a small block, generally after the first has been dyed.

*Bark yellow.* A mordant is used, the same as for red. The piece, when slightly dunged, is dyed about an hour with one pound of quercitron bark, the infusion being gradually heated during that time to 130° or 160°

*Berry yellow.* A decoction of French, or Turkey, or Persian berries, with half a pound of alum per gallon, is thickened with flour or gum; and the piece, when dry, is passed through a weak alkaline carbonate, or lime water.

*Verdigris green.* A solution of sulphate and acetate of copper is put on cloth, which is then passed through a strong solution of potash, in which some protoxyde of arsenic has been dissolved.

*Drab.* The same mordant as is used for purple. Bark, the dye stuff,

*Olive.* The chocolate mordant dyed in bark. Both these very much diluted, and thickened with gum.

*Buff.* A weak acetate of iron is applied, and washed in water.

3. *Chintzes.*—A number of different colours printed upon cloth together, viz. black, red, one or two pale reds, purple, blue, green, and yellow. The black, red, and blue, are the same as in No. 1.; the purple, as No. 1, thickened with gum; the two pale reds are weaker solutions of alum and acetate of alumina, thickened with gum; the yellow is berry yellow applied after the other colours are finished; the green is formed by the yellow falling upon the blue; and all the varieties of orange, olive, &c., by its falling upon the pale reds and purple. The dyeing and subsequent bleaching are the same as has been described in No. 1, with madder only.

4. *A dark ground discharged.*—When the discharge is printed before the mordant, it consists of concentrated lime juice alone, thickened with gum. The mordant, which is also thickened, is blotched over the whole piece, and dried off it as quickly as possible.

When the mordant is applied first it is not thickened, and the acid has an addition of one pound bisulphate of potash in each gallon. They are dunged and dyed like other single colours. Blacks, instead of madder, are generally dyed with logwood and galls.

5. *Blue grounds.*—To make a blue paste for dark blues, three to four pounds sulphate of copper are dissolved in a gallon of water, with a pound or a pound and a half of acetate of lead. The clear solution is thickened with pipe-clay and gum. The pieces printed with this paste are hooked upon a frame, and dipped in a weak blue vat five or six times; then taken out and kept in the air till they become blue. Alternate immersions and airings are thus continued till the requisite shade has been obtained. The goods are then washed and dipped in a weak sulphuric acid, to dis-

solve the oxyde of copper. The blue vat, as is well known, is made by one part of indigo, with two parts sulphate of iron, and about two and a half parts hydrate of lime.

6. A mordant for red, to resist the blue vat, is made by dissolving about four ounces acetate of copper in a red mordant, made from four pounds of alum, and two and a half pounds acetate of lead, per gallon, and thickening the solution with pipe-clay and gum. When this is printed upon the cloth and dipped in the blue vat, it resists the blue, and a white is left, which, when dunged and dyed in madder, becomes red.

A white called *neutral*, is made by dissolving sulphate of copper in concentrated lime juice, and is used along with this red. It must possess the three following properties : 1. Resisting the blue ; 2. Remaining white after dyeing, when the red happens to go over it ; 3. To leave no oxyde of copper upon the cloth.

A berry yellow is grounded in after the blue, white, and red, in this style, are finished.

7. *Chemical colours*.—This name has been given to those colours which are applied topically ; most of them are fugitive.

*Black*. A decoction of logwood and galls, thickened with flour, and, when cold, nitrate of iron mixed with it.

*Red*. A decoction of brazil or peach wood, with the protomuriate or permuriate of tin.

*Purple*. A decoction of logwood with muriate of tin.

*Blue*. Ground prussian blue is soaked in muriatic acid for a day or two, and then as much of it mixed with gum tragacanth water as is sufficient to give it the desired shade.

*Yellow*. A decoction of fustic with muriate of tin.

*Green*. A mixture of the blue and yellow.

All these colours are simply washed off in water.

M. Vitalis gives the following prescriptions in calico printing :—

#### *Mordant for Reds.*

- 52½ gallons of boiling water ;
- 150 pounds of pure alum ;
- 50 pounds of acetate of lead ;
- 6 pounds of commercial potash or soda ;
- 6 pounds of chalk ;
- 3 pounds of ground brazil wood.

Into a vat capable of holding 87½ gallons, and partly filled with the 52½ gallons of boiling water, the alum in powder is put, and then the decoction of brazil wood. After stirring till the alum is dissolved, the acetate of lead in powder is added. The mixture is to be carefully stirred for some time, and when the liquor begins to clarify, the potash

is put in, then the chalk, in small portions at a time, to avoid too great an effervescence. The whole must now be stirred for an hour, and left to settle. The clear liquor is used as occasion requires.

For strong reds (full reds) the above mordant is thickened with starch. This is called *first red*.

If reds of a weaker tone be wanted, the mordant is thickened with gum.

For the *second red* three quarts of the mordant are thickened with two pounds and a half of gum dissolved in a quart of cold water. The whole is well mixed by due agitation.

For the *third red* three pints and a half of mordant are mixed with the solution of five pounds of gum dissolved in ten pints and a half of cold water.

The above red mordant serves also for weld fustic and quercitron yellows, with all their shades.

#### *Mordant for Blacks.*

12 quarts of iron liquor, (pyrolignite of iron.)

4 ounces of copperas.

Dissolve the copperas in the liquor; and after having decanted the clear, mix in gradually four pounds of starch. Heat in a boiler, stirring continually, and take it out when the starch is well boiled.

#### *Another Black Mordant.*

For eight pounds of iron liquor, take about two pounds and a half of superfine wheat flour, which is to be gradually mixed up with a portion of the liquor; then add the remainder of this, and leave at rest for 12 or 24 hours, or even longer. Then boil for half an hour, or till the mixture has acquired the consistence of a paste. The boiler is then to be removed from the fire, and the mordant is to be stirred till it becomes cold. It is now to be passed through a sieve, and used in printing.

These mordants give a beautiful black with logwood, and especially madder.

Under the article Chemical Black, (topical black,) in Rees' Cyclopaedia, (article COLOUR,) we have the following recipes.

To a decoction of Aleppo galls, in five times their weight of water, made into a paste with flour, add a solution of iron in nitrous acid, of specific gravity 1.25, in the proportion of one measure of nitrate of iron to 18 or 20 of the decoction, and a black will be formed fit for almost all the purposes of calico printing, and possessing the chief requisites of this colour, namely, tolerable fixity, and a disposition to work well with the black.

When a nitric solution of iron is added to a decoction of galls, the

solution is decomposed, the oxyde of iron unites with the gallic acid and tanning principle, while the nitrous acid is disengaged. This appears from the blackness which the solutions assume immediately on being mixed. The disengaged acid, however, reacts in a short time on the new compound, the blackness gradually disappears, and if the nitrate of iron has been added in proper quantity, the paste in a few days becomes, from black, of a dirty olive green. When the proportion of nitrate of iron is greater than  $\frac{1}{16}$ , this change takes place sooner; and if it amounts to  $\frac{1}{8}$ , the paste, when applied to the cloth, will be a bright orange, like the acetate of iron. By exposure to heat and air this colour generally deepens, becoming grey, and at last a full black. In this state it is permanent, and adheres powerfully to the cloth.

These changes of colour depend on the solution of the tannate and gallate of iron in the disengaged nitrous acid, and the dissipation of the acid from the cloth, when it is exposed to heat and air. This solution of the tannate and gallate of iron is indeed an essential requisite to the goodness of the chemical black. If the disengaged acid is not sufficient to effect this, or if it is in a state of too great dilution, the colour has but a feeble adherence to the cloth. It is not presented in a state favourable to its union with it, since the combination into which the iron has entered is insoluble in water. It lies merely on the surface, but does not penetrate its fibres, and gives way readily in the various operations to which it is subjected. This chemical black, therefore, is a solution of the tannate and gallate of iron in nitric acid.

#### MORDANTS FOR VIOLETS, (FROM VITALIS.)

*First violet.*—16 quarts of iron liquor;

8 quarts of water;

4 ounces of Roman vitriol, (sulphate of copper.)

This mixture is to be thickened with powdered gum, in the proportion of a pound to the quart.

*Second violet.*—Mix three parts of the preceding with one of water, and thicken as above.

*Third violet.*—Dilute two parts of the first mordant, with three of water.

#### Coffee Colour.

10 quarts of iron liquor;

2 quarts of the mordant of the *first red*;

4 quarts of water.

Thicken with starch.



*Puce, or Carmelite Colour.*

3 quarts of mordant of the *first red* ;  
1 quart of iron liquor.

*Deep Brown.*

2 quarts of red mordant ;  
1 pint of iron liquor.

*Maroon Colour (Chestnut-Brown.)*

2 quarts of violet mordant ;  
1 quart of red mordant ;  
8 ounces of green copperas to be dissolved in the  
mixed mordants.

*Chocolate.*

8 quarts of violet mordant ;  
12 quarts of red mordant.

*Deep Lilac.*

1 quart of violet mordant ;  
1 quart of mordant for the second red.

*Pale Lilac.*

1 quart of violet mordant ;  
3 quarts of mordant of the second red.

*Musk Colour.*

1 quart of red mordant ;  
3 quarts of black mordant.

*Incarnate (Flesh) Colour ; Colour between Cherry and Rose.*

10 quarts of red mordant ;  
1 quart of black mordant.

*Olive Colour.*

Welding on the mordant of the first, second, or third violet.

*Réséda Colour.*

Welding on puce mordant.

## COLOURS OF APPLICATION (TOPICAL COLOURS) FROM VITALIS.

*Topical, or Pencil Blue.*

Boil in 15 gallons of water, for half an hour, 15 pounds of potash, and six pounds of quicklime, in order to render the potash caustic. Then add

six pounds of orpiment (sulphuret of arsenic) reduced to fine powder, and continue the boiling for a quarter of an hour; taking care to stir continually with a rod. When the boiler is a little cooled, pour into it from six to eight pounds of indigo well ground at the mill, and stir again till the indigo be well dissolved, which is discovered by a drop of the liquor, when placed on a bit of glass, appearing yellow. The bath, while still hot, is to be thickened with a pound of gum for every three pints and a half of liquor, or with eight ounces of starch.

This preparation must be carefully preserved from contact of air, and only employed when its colour is yellow, or at least, yellowish-green. If it become blue, the liquor is to be treated anew with some pounds of caustic potash and orpiment.

This blue of application, says M. Vitalis, much used formerly, is seldom employed at the present day. Another blue, of less permanence, but more brilliancy, is now preferred. It is made with prussian blue, in the following manner :—

Into an earthen pot, four ounces of finely ground and sifted prussian blue are to be put. Over this must be slowly poured, stirring all the while, sufficient muriatic acid, to bring it to the consistence of syrup. The mixture is to be stirred every hour for a day, and afterwards thickened with from 14 to 28 pints of gum-water, according to the shade wanted.

#### *Topical Red.*

A pound of brazil wood is to be boiled in seven pints of water for two hours ; the decoction is then to be decanted, and boiled down to three pints and a half. As much red mordant must now be added as is necessary to form a fine red ; and it is to be finally thickened with eight ounces of starch. The colour will be more beautiful the older the decoction of brazil wood is.

Instead of brazil wood, wood of Japan, Saint Martha, or Nicaragua (peach wood,) may be used, provided their colour has been refined from the dun which they contain, by the process with milk, previously described under note PP.

#### *Topical Yellow.*

This is prepared by boiling four pounds of Turkey or Avignon berries in five gallons and a quarter of water, which is boiled down to one-half. The clear liquor is drawn off, and a pound and a half of alum is dissolved in it. For the light yellows it is thickened with gum ; for the deep with starch. This topical yellow does not resist soap. The following is equally fast and agreeable.

In two gallons of water boil four pounds of quercitron bark in powder,

down to one-half of the bulk. Pass through the searce, thicken with three pounds of gum, and mix in gradually enough of solution of tin to render the colour of a brilliant yellow. This yellow resists vegetable acids and soap very well. When placed on a blue ground, it forms a fine green, and it may be applied by the plate or the pencil.

The best solution of tin which can be employed for this topical yellow, is that made with a mixture of three ounces of muriatic acid, four ounces of nitric, and four ounces of pure water. Two ounces of grain tin are to be dissolved bit by bit in this liquor. When the solution is completed, half an ounce of sugar of lead is to be added. The mixture must then be well stirred ; left to settle, and decanted. Half an ounce of this solution is to be taken for every quart of the yellow bath.

On mixing with the yellow bath a little of the annotto bath, we have orange yellows.

#### *Rust-Yellow.*

This is made with acetate of iron, or the *black cask*. It is thickened with gum for the light yellows, and with starch for the deeper shades. Rust-yellow, when applied on blue, gives a deep green, which serves for the stems of certain flowers.

#### *Topical Green.*

This preparation is formed by a mixture of topical blue and yellow, in which the yellow predominates considerably. The mixture must be made by little and little with the utmost care, so as to hit the wished-for shade.

#### *Topical Aurora.*

A sufficient quantity of alum in solution must be added to the annotto bath ; and the mixture is to be thickened with gum.

#### *Topical Black.*

To three gallons of the black cask, or of pyrolignite of iron, at 4° Baumé (5½° Tw.) add four ounces of Roman vitriol dissolved in water, and a sufficient quantity of decoction of galls to form a good black. Thicken with three pounds and a half of starch, which is to be gradually worked up with a portion of the liquor. Boil, withdraw from the fire, and keep stirring, till the liquor be cool ; it must then be passed through a searce or a linen cloth.

#### *Another Topical Black.*

In six gallons of water, boil two pounds of logwood, two pounds of sumach, and eight ounces of galls, till the liquor be reduced to half its volume. Add then a quart of the black cask (or pyrolignite of iron ;) boil away

six quarts; take off the clear of the bath, dissolve in it two ounces of Roman vitriol, and one ounce of sal ammoniac; after which thicken with starch, and pass through a search before making use of the composition.

*Topical Violet and Lilac.*

In seven gallons and a half of water boil six pounds of logwood, ground or in chips, till ten quarts be evaporated; (*jusqu'à réduction de dix pintes.*) Decant the clear, and dissolve in it one ounce of alum for every quart of liquor. The deep violets are thickened with starch, and the light violets with gum, which is to be dissolved in the cold.

This colour changes readily; for which reason it should be prepared only as wanted, and be immediately put to use.

EXAMPLES FROM VITALIS OF THE MODE OF MANAGING DIFFERENT STYLES OF CALICO PRINTING.

*Calicoes of one Block (Indiennes à une main.)*

*First Example.*—Violet on a white ground.

1. Impression of violet mordant; 2. Dunging and washing; 3. Madder; 4. Branning and exposure on the grass for a few days, to clear the grounds.

*Second Example.*—Black on a yellow ground.

1. Bath of yellow mordant; 2. Welding; 3. Topical black.

*Calicoes of two Blocks.*

*First Example.*—First olive and second olive on a white ground.

1. Impression of the first olive mordant; 2. Impression of the second olive mordant: 3. Welding.

*Second Example.*—Red and blue on a white ground.

1. Impression of the red mordant: 2. Madder; 3. Impression by the block (*rentreur\**) of topical blue.

*Third Example.*—Yellow and black on a white ground.

1. Impression of the yellow mordant, welding; 2. Impression of topical black.

*Calicoes of three Blocks.*

*Example.*—First olive, second olive, and yellow on a white ground.

1. Impression of the first olive mordant; 2. Impression of the second olive mordant; 3. Impression of the yellow mordant; 4. Welding.

\* When the calico is to have several colours, says M. Vitalis, for example, black, several reds, several violets, &c., as many mordants must be given as there are different colours, which must be inserted (*rentrés*) into the first plate (*figure*), called the plate of impression (printing block, *planche d'impression*.)

The insertion (*rentrage*) of the mordants is executed by means of blocks (*planches*),

The third block (*main*) might also be performed by the impression of the topical yellow.

*Calicoes of four Blocks.*

*Example.*—Black, red, violet, and yellow on white.

1. Impression of the black mordant; 2. Impression of the red mordant; 3. Madding; 4. Impression of topical yellow, or of the yellow mordant, and welding.

*Calicoes of five Blocks.*

*Example.*—Black, red, violet, yellow, and blue.

1. Impression of the black mordant; 2. Impression of the red mordant; 3. Impression of the violet mordant; 4. Madding, insertion of the blue, and afterwards of the yellow.

*Calicoes of six Blocks.*

*Example.*—First olive, second olive, black, first red, second red, and yellow on white ground.

1. Impression of the black mordant; 2. Impression of the first red mordant; 3. Impression of the second red mordant; 4. Madding; 5. Impression of the second olive mordant; 6. Impression of the yellow mordant; 7. Welding.

It is now very seldom, however, that the number of three blocks (courses) is exceeded, on account of the high price to which the labour would necessarily raise the calico.

The following is an example of printing in fugitive colours :

Violet, black, red, and yellow, on white ground.

These four topical colours are successively applied, in the order above mentioned.

Calicoes with fast colours, after receiving the impressions, are dried, and washed from the mordants, when they are ready for the madding.

which take the name of *rentreures*. These blocks are engraved with the same patterns as the printing blocks, but so as that they apply the new mordants only to the places of the pattern reserved in the first blocks. It may be readily conceived how necessary it is for these blocks to have an exact correspondence with one another, otherwise the colours would not be comprised within the limits of their outlines. This fault is too often met with in common prints, on account of the rapidity with which they are worked off, and the little care taken in the fabrication. In order that every colour may occupy the place assigned to it in the drawn pattern (*le dessin enluminé*), adjusting brass points (*picots de rapports*) are made use of, which guide the printing on of the successive mordants, at precisely that place of the figure where the colour to be produced from each mordant ought to fall.

*Of Printing by Reserves, (with Reserve or Defending Pastes.)*

Goods printed by reserve, are so called, because the colour does not strike the whole surface, but only certain unprotected portions of it.

The reserve is composed of the reserve bath, and the thickening.

*Reserve Bath.*

Dissolve in a quart of water six ounces of sulphate of copper, three ounces of verdigris, two ounces of alum, and four ounces of gum arabic.

*Another Reserve Bath.*

Dissolve in three pints and a half of water four ounces of Roman vitriol (sulphate of copper,) and six ounces of verdigris, to which add one pound of gum arabic; and when it is dissolved, pass through a fine sieve, or let it settle, and decant.

*Thickening.*

To thicken the bath, knead a pound of pipe-clay, well ground and sifted, with three or four ounces of water: with this thick dough carefully mix the reserve bath, and triturate well before making use of it.

The reserve is printed on the goods like the mordants. Twenty-four hours after the impression the goods are to be passed through the dyeing vat. This style is much used in blue dipping.

The theory of the reserve is very simple. The oxyde of copper, which forms the basis of the reserve, restores to the indigo the oxygen which it had been deprived of by the sulphate of iron. The re-oxydised indigo loses its solubility, and consequently cannot fix on the stuff.

Since the reserve, intended to nullify the action of the indigo, essentially acts merely by the oxyde of copper which it contains, it follows, that the proportions of this oxyde are not indifferent, and that the measure will not perfectly accomplish its end, unless the dose of oxyde of copper, which the sulphate, &c., can furnish, be adequate to neutralize the action of the indigo. A similar result would ensue, if the reserve be not suitably thickened.

Some object to the introduction of alum.

The proportions of the cupreous salts ought, however, to be as little as can effect the purpose; if their quantity be too great, their operation would be extended to the indigo diffused through the bath.

Sometimes the sulphate of copper is made to predominate, and sometimes the acetate.

The following recipes for reserves are given by M. Vitalis:—

1. Sulphate of copper	.	.	.	.	20 pounds
Acetate of copper	.	.	.	.	12

Gum . . . . .	16 pounds
Alum . . . . .	5
Water . . . . .	7 gallons
2. Sulphate of copper . . . . .	16 pounds
Acetate . . . . .	24
Alum . . . . .	4
Gum . . . . .	15 lbs. 8 oz.
Water . . . . .	1 $\frac{1}{2}$ gallons

The thickening is always made with pipe-clay.

*To make a Sky-blue on a Dark Blue.*

1. Dye the cloth of a sky-blue ; 2. Apply the usual reserve ; 3. Pass the cloth through a strong blue vat. Brighten in a bath, feebly acidulated with oil of vitriol, (or muriatic acid), to carry off the particles of lime suspended in the vat. Wash and dry.

*Sky-blue, Dark Blue, and White.*

1. Apply the reserve ; 2. Dye sky-blue ; 3. Apply the reserve anew ; 4. Pass through a blue vat of sufficient strength.

*Deep Blue, Sky-blue, Green, Yellow, and White.*

1. Print on the reserve : 2. Pass through a weak vat, giving two or three dips ; dry, brighten with very dilute sulphuric acid, wash, dry again ; 3. Print on once more the common reserve paste ; 4. Dye in a stronger vat than the above, till the blue be sufficiently deep ; dry, brighten as before, wash and dry ; 5. Print on the red mordant, and dry ; 6. Give the weld or quercitron. The mordant applied to the white spots, and to the pale blue, (*petit blanc*), affords yellow and green. The white portions that have not been touched with the mordant remain white, in like manner as the pale blue spaces, not covered by this mordant, furnish the pale blue.

Reserves are also applied to silks.

For example, on the handkerchiefs called *foulards*, the reserve is styled *waxing*.

A mixture of tallow and rosin is melted, and applied to the silk with the block ; this reserve being given, the silk is dipped in the blue vat. The reserved portions being defended from the action of the indigo, remain white, while the rest of the surface takes a fast blue.

*Sky-blue, Red, and White.*

1. Apply the usual reserve ; 2. Apply the red mordant, thickened with pipe-clay, and dry ; pass through a weak blue vat, to obtain sky-blue ; wash at the river, madder, wash, and spread out on the grass to clear the white.

*Printing with Discharges (par rongeant) on a Mordant.*

This process serves to form mourning garments, composed of a white figure on a black ground.

The piece of goods is first passed through the black mordant, (by means of the padding or blotching machine.) When this mordant is very dry, (by passing, for example, over steam cylinders,) the white discharge is applied, prepared with nitric, oxalic, tartaric, or citric acid, or bisulphate of potash, thickened with British gum. It is dried, washed, and madder. On quitting the madder bath, the goods must be well washed, and exposed on the grass till the whites be very clear.

The portions of the cloth where the mordant has not been acted on by the discharge, will take a black of a greater or less depth from the madder, while on those places where the discharge has been applied, the mordant will be removed, and the madder colour will not combine with the stuff. Exposure on the grass will carry off the loose madder.

In like manner, by this process, white figures may readily be obtained on a ground of red, carmelite, violet, puce, &c. ; since it will be necessary merely to pass through the mordant of one of these colours, then to apply the white discharge, and finally to madder.

To have white figures on an olive ground, weld or quercitron must be used instead of madder.

*Printing with a Discharge on Colour, (Dyed Goods.)*

Suppose that the calico has been dyed in a logwood bath, mixed with iron liquor, the cloth will take a black colour. If, after dyeing, it be impressed with a solution of tin, properly thickened, the ferruginous portions of the cloth touched with the discharge will be removed, and they will pass from a deep black to a very brilliant crimson.

By subjecting to the same treatment calicoes dyed of different colours and shades, determined by the different degrees of oxydizement of the iron, a multitude of varieties will be produced, either in the colours or in their shades.

By a similar operation, we may make figures of a beautiful green on goods, by dyeing them first of a pale blue in the indigo vat, passing them then through a bath of sumach and sulphate of iron, and finishing in a bath of quercitron with alum.

Here the green colour produced by the indigo and the quercitron remains masked, as well as the other colours, by the oxyde of iron in the sulphate, till the solution of tin be applied, which causes the other colours to disappear, and gives to those that remain a lustre which they would not otherwise have had ; because the solution of tin renders the quercitron



yellow more vivid, and because from this vivid yellow, associated with the blue, results a more brilliant green.

A figure of aurora colour on an olive ground may be made, by passing the cloth first through a bath of sumach and sulphate of iron, then washing in an alkaline decoction of fustet, and printing on at last the solution of tin.

Let us give for an example the mode of making yellow figures on olive. The problem is reduced to find a discharge, which, in destroying the colour communicated by iron, can at the same time change the colour to yellow. This discharge is the thickened solution of tin. To the solution of salt of tin (muriate) a little muriatic acid is added. This is thickened with starch, previously boiled, in a very thick and cold state, observing to pour in the solution in small portions, in order to ensure the thorough union of the ingredients. As soon as the piece has been impressed with this discharge, it is carried to the river to be washed, and to prevent the discharge from acting too long on the colour. If the pattern required is black, it would be necessary to apply it before the yellow discharge.

*Calico Printing by the combined Methods of Discharges on the Mordant and on the Dye.*

First Example.—Olive, yellow, and white.

1. Pass through the olive mordant. 2. Print on the white discharge; wash and dry. 3. Weld. 4. Print on the yellow discharge.

Second Example.—Bright red, and dull red; white, yellow, and black, on an olive ground.

1. Print on the red mordant, 2. Madder, 3. Pass through the olive mordant. 4. Print on the white discharge. 5. Weld. 6. Print on the yellow discharge and the topical black, and wash.

The colours by discharges, though bright, are not so fast as those given by the dye-baths.

If, instead of applying the yellow discharge, thickened as usual with starch, one-third more starch be employed, and a colouring of decoction of Turkey berries, or brazil wood, be added, we shall obtain, in the first case, a richer yellow, and, in the second, an orange-yellow.

*Of Lapis Lazuli.*

This name is given to calicoes which, after having been printed with reserve discharges, and different mordants, are passed in succession, first through the blue vat and then through a madder bath. If a yellow or a green be wanted, there is given, in the sequel of the madder washing, a yellow mordant, and the goods are turned through a bath of weld or quercitron.

Suppose that we are to print on cloth a pattern into which there enter white, red, black, blue, green, and yellow. The goods being previously thoroughly whitened, we proceed as follows :—

1. Apply the reserve discharge.\* 2. Print on the red mordant, thickened with pipe-clay. 3. Print on the black mordant, thickened in the same manner. Pass the goods through a strong vat in forty-eight hours at farthest after the printing has been given. The dipping ought to be for six minutes at most, at two times : between each dip, the goods must be aired for five minutes. They are then carried to the river, allowed to steep in it for an hour, and washed. 5. They are dunged. 6. Passed through bran. 7. Madderred. 8. Beetled very carefully, and dried. 9. The red mordant is applied, which serves also as a yellow mordant. The pieces are now to be well cleaned. 10. They are passed through a quercitron bath, after which they are washed and finally dried.

The lapis pattern may be put on a blue ground, a red, puce, &c. ; whence result a great many varieties. The pattern was originally called *lapis*, from its resemblance to *lapis lazuli*. A slight reflection on the above process will show us how the different colours are produced.

The blue is the immediate effect of the blue vat ; the red and black are developed by the maddering on the respective mordants of these colours. The combination of blue with yellow, on the yellow mordant, gives green. The yellow results from the colouring matter of the quercitron bark fixed by the red mordant, which is, at the same time, the mordant for yellow. Finally, the white is occasioned by the white discharge of the reserve discharge.

A neat and expeditious style of discharge work on indigo grounds, has, of late years, been extensively employed by the calico printers in this country. A paste is made with aquafortis and pipe-clay, which is applied in the press, by a revolving cylinder of wood, having the pattern cut upon it. The cloth, immediately after receiving the impression, is passed through a strong body of steam, at 212° Fahr., issuing from a row of small orifices in a horizontal box. The high temperature gives blanching energy to the nitric acid, and the accompanying moisture dilutes it, so as to prevent corrosion of the cotton fibres. The safety of the goods, however, is ensured by a thorough washing.

\* The reserve discharge is prepared by melting together hog's-lard and rosin, (*arcanson*) and when the mixture is cool, diluting it with oil of turpentine ; adding afterwards binarsenate of potash, and a little corrosive sublimate in powder. The whole being well blended or ground together, is to be then printed on.







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